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IRA REMSEN

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STEREOISOMERISM AND THE LAW OF ENTROPY.

BY ARTHUR MICHAEL.

Louguinine[1] determined in 1888 the heat of combustion of maleic, fumaric, citraconic, and mesaconic acids and found the value for maleic and citraconic acids to be greater than that for their stereomers. Stohmann,[2] in the course of his brilliant thermochemical investigations, repeated these experiments, and concluded, after examining the heats of combustion of other stereomeric substances, that the unstable modification has a greater heat of combustion, and further, it loses energy in changing into the stable stereomer.

Klinger[3] first suggested that isomers with identical molecular weight and chemical structure, yet with different amounts of energy, may exist, and he later[4] designated such isomerism as alloergaty. As this chemist believed that we have no sure knowledge in regard to the spatial arrangement of the atoms in stereomers, he classed these substances as examples of alloergaty. Subsequently, Tanatar[5] discussed the subject independ-

[1] Compt. rend., **106**, 1289.

[2] J. prakt. Chem., N. F., **46**, 531.

[3] Ber. d. chem. Ges., **11**, 1026 (1878).

[4] *Ibid.*, **32**, 2194 (1899).

[5] Ann. Chem. (Liebig), **273**, 54 (1893).

ently, and suggested that the spatial arrangement of the atoms and their dynamic condition in stereomeric substances may be correlated, or that a class of isomers may exist, which, although stereomerically identical, contain, notwithstanding, different amounts of energy in their molecules. The latter kind of isomerism Tanatar designated as energy or dynamic isomerism. While it is absolutely certain that a considerable number of isomeric substances cannot be grouped according to the present stereoisomeric classifications,[1] and that some of these substances are remarkably sensitive to the influence of physical and chemical energy, it would seem that little or nothing could be gained at present by the introduction of such views into chemical theory, as these speculations are very vague and their adoption would lead to many unproven, and in some cases improbable, conclusions. On the other hand, the development of any theory of stereoisomerism certainly necessitates the acceptance of Stohmann's rule as a basis in an endeavor to connect the chemical properties and reactions of stereomeric substances with their energy relations. In this way we may succeed in developing a theory based on the fundamental chemical principle known as the law of entropy. At once a very serious obstacle is met with in the meagre thermochemical data which exist on the heat of combustion of stereomeric bodies. It is therefore extremely important for the theory of stereoisomerism that Stohmann[2] has proved that the heats of combustion of isomeric unsaturated acids and their coefficients of conductivity in aqueous solution stand in a direct relationship to one another. *In all cases of stereomeric unsaturated acids, where both these values are known, the same relationship holds true*, and if we make the extremely probable assumption that the proportion of free energy in stereomers, *i. e.*, that part of their whole energy which is freely changeable into other forms, to their bound energy increases directly with the heat of combustion, then not only their properties, but also a considerable number of stereomeric reactions, may be brought into correlation with the law of entropy.

[1] Compare Michael: Ber. d. chem. Ges., **39**, 210.

[2] J. prakt. Chem., N. F., **40**, 358; **46**, 530.

Kekulé,[1] in his memorable paper "Ueber die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," assumed that the first stage in every reaction consists in two molecules attracting each other through their chemical affinity, forming a sort of loosely joined larger molecule, and that in this process the coherence of the atoms decreases, since part of their energy is used up in this mutual attraction by the atoms of the other molecule. Kekulé also assumed that neighboring molecules of the same kind help to decrease the attraction of the atoms of the unlike molecules. In this way he explained mass action as occurring when the molecules that act catalytically are the same as one of the components of the large molecule, and catalysis when they are of a different nature from either of them.

This practically forgotten conception was revived some years ago, and attention was called to its extreme importance in explaining chemical changes.[2] According to the writer, the "Kekulé double molecule" is formed by the attraction of the free energy in two or more unlike molecules, and its formation proceeds with the conversion of more or less of the free energy into bound energy and heat, its stability being determined in this way. Such double molecules are represented by compounds with water of crystallization or by the numerous addition products of saturated organic substances with halhydric acids and halogens.[3] The second stage in chemical action may occur in one of three ways: (*a*) by a double molecule passing over, with further conversion of the free into bound energy, into a much more stable ordinary molecule, a process represented by an addition reaction; (*b*) by a homogeneous; and (*c*) by a heterogeneous double decomposition.[4]

In applying these views to explain the catalytic action of a small amount of hydrochloric acid in converting a large amount of maleic into fumaric acid, we may imagine a system consisting of one molecule of the mineral and a large number of molecules of maleic acid. The first step would be the formation of a double hydrochloric-maleic acid molecule. A more complete addition to form chlorsuccinic acid is impossible for two reasons: firstly, because the surrounding molecules of maleic acid are exerting a strong attractive force on the double molecule in their endeavor to decompose it and to unite in their turn with the liberated hydrochloric acid; and secondly, because the increase of entropy produced by the formation of a single molecule of chlorsuccinic acid would be very slight in comparison with that accompanying the conversion of all the maleic into fumaric acid.[1]

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[1] Ann. Chem. (Liebig), **106**, 141.

[2] Michael: Ber. d. chem. Ges., **34**, 4028; **39**, 2139.

[3] See *Ibid.*, **39**, 2570.

[4] Homogeneous is used in the sense that the original substances are reformed, and heterogeneous, that new chemical products are formed in the double decomposition. The first process may occur between a substance and a solvent, and is then the cause of the phenomenon known as electrolytic dissociation. See J. prakt. Chem., N. F., **60**, 429; Ber. d. chem. Ges., **39**, 2570.

Since the change maleic → fumaric acid is entropic, we may assume, from a theoretical standpoint, that this reaction is proceeding at ordinary temperature; in order to effect a rapid conversion, we must in some way increase the free energy—which is the deciding factor in the transformation—in maleic acid.

This is what is actually done in the formation of the double molecule, which brings about the concentration of almost all of the free energy in separate molecules of hydrochloric and maleic acids into this double molecule. Now, as the greater free energy of maleic acid over that of fumaric acid shows itself in a greater additive power for hydrochloric acid, it is obvious that the hydrochloric-fumaric acid double molecule could have only a transient existence under these conditions, for it would be decomposed by the maleic acid present. The above processes would be repeated until all the maleic acid is converted into fumaric acid, thus realizing the maximum increase of entropy under the conditions of the experiment.[2]

Some interesting experiments on the conversion of maleic into fumaric acid have been published by Skraup,[3] who found that hydrogen sulphide or sulphur dioxide, alone, do not change maleic acid in aqueous solution, but when they are used together, a conversion into fumaric acid is partially brought about, that is, the transformation only occurs at the moment of their chemical interaction; he found also that in the action of hydrogen sulphide on certain metallic salts of maleic acid the same conversion is partially effected.[1] Skraup noticed that these reagents are absorbed to a greater extent by an aqueous solution of maleic acid than by the same amount of water, thus indicating the formation of a loose addition product.[2] Assuming this to be the case, and that the double molecule of maleic acid with hydrogen sulphide reacts exothermically with sulphur dioxide or with its double maleic acid molecule, as these substances do in the absence of the acid, we obviously have conditions more favorable for the conversion of maleic into fumaric acid than if the energy were not liberated through the interaction of these double molecules.

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[1] It is in agreement with this explanation that if the mineral acid is used in considerable quantity, a mixture of halogen-succinic and fumaric acids is obtained.

[2] This explanation of catalysis is capable of a very general application in organic as well as inorganic reactions.

[3] Monats. Chem., **12**, 107.

The same explanation may be applied to the formation of fumaric acid in the decomposition of metallic maleinates by hydrogen sulphide; the first stage in the reaction is the formation of a double molecule of the salt with hydrogen sulphide, and the energy liberated in its decomposition into metallic sulphide and maleic acid is obviously readily available to facilitate the exothermic change of maleic into fumaric acid. It is also of interest that Skraup found that a very much greater proportion of fumaric acid is formed when the copper, lead, and cadmium salts are decomposed than in the case of the zinc and nickel salts. Judging by analogy from thermochemical data on the decomposition by hydrogen sulphide of other salts of these elements, this is what we should expect, as the heat of formation of the sulphides is greater for the metals of the first than for those of the second group.

A very important factor in determining the extent and facility of the transformation of maleic into fumaric acid lies in the much greater insolubility of the latter acid. The question of the formation of an insoluble or volatile substance, and its elimination, owing to these properties, from a chemical system which otherwise would be in a condition of reversible equilibrium, may determine the entropy, and in this way the course of a reaction; obviously the same relations must prevail when the equilibrium between two stereomeric bodies is similarly disturbed. Thus, if molten maleic acid (130°) passes over partially into fumaric acid, and at a certain temperature a condition of reversible equilibrium is established, the fact that the latter acid is insoluble in the flux and possesses a higher melting point (258°) would, as long as the flux is kept under that temperature, necessarily lead to a complete conversion into that acid. On the other hand, if we have fumaric acid in a state of flux, the question of insolubility as an entropic factor in determining a chemical change would be eliminated, and that of volatility would arise instead; therefore, in the conversion of fumaric acid into maleic acid at a high temperature and of this into its still more volatile anhydride and water, we have an illustration of the tendency to the formation of volatile as well as endothermic compounds under such conditions.

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[1] Skraup (*Loc. cit.*, p. 146) assumes two kinds of intramolecular gyration and that certain exothermic reactions may act catalytically by a sort of chemical resonance. Such very indefinite and unlikely conjectures do not contribute to a better understanding of these phenomena.

[2] *Ibid.*, p. 140.

The stereomeric relations that occur in addition processes are extremely complicated; outside of the group of dibasic, unsaturated acids, they have been best studied with crotonic and cinnamic acids and their derivatives, and some of the reactions in these groups of substances will be considered in connection with the energy relations.

As far as we know, the addition of hydrobromic acid to propylene may proceed with the formation of either propyl bromide or isopropyl bromide, without any structural opposition to its going either way. That it actually occurs in the direction of the maximum increase of entropy, that is, with the formation of isopropyl bromide, agrees with the theory.[1] If we only had the same insight into the differences in the intramolecular arrangement of the atoms in stereomeric bodies as we have into those of structural isomers, and could connect these relationships with the quantity of energy contained in such stereomers as we can with isomeric substances, we should undoubtedly be able to place stereomeric reactions on a much more satisfactory theoretical basis. There will, however, always remain a notable difference between the reactions of structural and of stereomeric substances,[1] as very slight changes in the conditions of the experiment may, in the case of stereomeric compounds, obscure the true nature of the process; the only product which can be isolated may not be the actual primary product but a stereomerized secondary derivative.

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[1] Michael: Ber. d. chem. Ges., **39**, 2140; J. prakt. Chem., N. F., **68**, 499.

These conditions in stereomeric reactions partially account for the difficulty in developing the subject consistently from a theoretical standpoint. Thus the addition of chlorine to maleic and fumaric acids leads to the formation of stereomeric dichlorides; we also know that it is much more difficult to convert maleic acid dichloride into fumaric acid dichloride than maleic acid into fumaric acid. From this relationship we may conclude that there exists in maleic acid dichloride some entramolecular obstacle to overcome which requires considerable energy, and it thus prevents the free progress of the reaction to the maximum increase of entropy which undoubtidly would be represented by the formation of fumaric acid dichloride. Cinnamic acid corresponds to fumaric acid in its physical properties and stability towards reagents that do not change its chemical composition; nevertheless, chlorine forms with it in the dark[2] or in light free from actinic rays[3] a low melting dichloride; in sunlight, on the contrary, only a higher melting stereomer is formed. Since these addition products stand in the same relation to each other that maleic acid dichloride does to fumaric acid dichloride, we are forced to the conclusion that cinnamic acid and chlorine give a maleinoid addition product as the primary result. How can we explain this remarkable effect of sunlight in effecting, even if the experiment is made in the cold, so complete a conversion of the lower into the higher melting dichloride that the first product escaped detection until the addition was made in the dark? There are two explanations:

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[1] This statement is made with the reservation that desmotropic structural isomerism is excluded.

[2] Liebermann and Finkenbeiner: Ber. d. chem. Ges., 28, 2226.

[3] See the following paper.

We may suppose that the double molecule of cinnamic acid and chlorine, unassisted by actinic energy, can form only the ordinary cinnamic acid allodichloride molecule; but at the moment of the change of double into single molecule and with the help of actinic rays, it then possesses sufficient chemical momentum to realize, in the formation of the higher melting dichloride, the maximum condition of entropy; or, what seems a less probable explanation, it may be that only in actinic light can the allodichloride unite with chlorine to form a double molecule, and that this possesses the free energy necessary to cause the entropic change into cinnamic acid dichloride and chlorine. An experimental confirmation of either of these interpretations is by no means impossible; at present, however, much greater importance is to be attached to the fact that the primary as well as the final product in stereomeric addition reactions is dependent on the chemical nature of these bodies, and also on that of the additive substance—in other words, on the entropy of the reaction[1]—and that this relationship effectively debars all mechanical explanations of these changes.[2]

The differences between the stereomeric results obtained by additions to fumaric, maleic, and cinnamic acids also appear in the corresponding acetylene acids, but since stereoisomerism in the latter series does not exist, the possibility of a stereoisomerization by the additive reagent before the addition process occurs is here excluded. Acetylenedicarboxylic acid and hydrobromic acid give the higher melting, chemically more stable and more entropic of the two stereomers, that is, bromfumaric acid, as direct product of the reaction; with phenylpropiolic acid a mixture of two β-bromcinnamic acids[3] is obtained, consisting largely of the product melting at 157°, which, although it has a higher melting point than the other β-brom acid (134°), gives allocinnamic acid on reduction.[4] To what extent this result depends on the nature of the additive reagent is seen when acetylenedicarboxylic and phenylpropiolic acids are reduced in

[1] Michael: Ber. d. chem. Ges., **34**, 3646.

[2] J. prakt. Chem., N. F., **75**, 117.

[3] Michael and Browne: Ber. d. chem. Ges., **19**, 1378; **20**, 550.

[4] Liebermann and Scholz: *Ibid.*, **25**, 951.

aqueous solution with zinc, for here the results are comparable, fumaric and cinnamic acids being formed. These last additions proceed, therefore, according to the relations of maximum entropy, for we know that these acids contain considerably less energy than their alloisomers.

Unfortunately, we are not at present in possession of any data which enable us to connect the peculiar behavior shown by phenylpropiolic and cinnamic acids towards hydrobromic acid and chlorine with the energy relations developed in the addition products formed. We do know, however, that energy supplied by halhydric acids, or in the form of heat, may give the chemical momentum necessary to realize the transformation of a maleinoid into a fumaroid acid, when the first-named product shows the greater acidity; also, that the more acidic of these stereomers shows the greater solubility in water. It is of interest, therefore, to trace the connection between the halogen derivatives of the crotonic and cinnamic acids and these relations. The α-monohalogen derivatives of the stereomeric crotonic and cinnamic acids[1] exhibit a behavior analogous to that of the unsubstituted acids; the lower melting stereomer possesses a decidedly greater acidity constant,[2] is more soluble, and when heated or treated with halhydric acids passes over into the higher melting fumaroid derivative. Of the two β-chlorcrotonic acids, the higher melting product (94°) is formed on the addition of hydrochloric acid to tetrolic acid,[3] and gives crotonic acid on reduction. Notwithstanding these properties, it has a larger acidity constant[4] than β-chlorisocrotonic acid, (59°) and therefore should contain a greater amount of free energy. In accordance with this relationship of their respective energies, the higher melting, apparently fumaroid β-chlorcrotonic acid is convertible by heat into the lower melting β-chlorisocrotonic acid, and is also the more soluble[1] of the two stereomers.

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[1] Michael: J. prakt. Chem., N. F., **52**, 345.

[2] The value for α-bromcinnamic acid (130°) is quoted as 1.44, and that of its stereomer (120°) as 0.093, obviously an inverse relationship to that stated above. This contradiction is due to a curious mistake made by Ostwald (Z. physik. Chem., **3**, 278). In his first paper (J. prakt. Chem., **32**, 367) the classification of Barisch (*Ibid.*, **20**, 185) is accepted as correct: that is, the acid melting at 130° is considered as a β, and that melting at 120° as an α derivative. In this paper, Ostwald shows that the latter acid is considerably more acidic and explains this fact by a greater proximity of halogen to carboxyl. In his subsequent paper, he uses the Glaser classification (Ann. Chem. (Liebig), **143**, 330), which is the opposite to that of Barisch, although the experimental results are still given according to the views of Barisch.

[3] Friedrich: Ann. Chem. (Liebig), **219**, 370.

[4] Ostwald (Z. physik. Chem., **3**, 245). This investigator emphasizes the apparent discrepancy in the acidity constants of these acids.

The addition of hydrobromic acid to phenylpropiolic acid gives principally the β-bromallocinnamic acid melting at 159°, which is reducible to allocinnamic acid,[2] and is also convertible by heat into the lower melting (134°) stereomer.[3] These relations agree with those in the crotonic series in the sense that, contrary to those holding for the mother substances and their α-halogen derivatives, the higher melting β-halogen acid goes over on heating into the lower melting stereomer; unfortunately, the acidity values in the cinnamic series have not been determined, so that the connection between these factors and stability towards heat cannot be traced.

It has already been stated that the reactions of stereomeric isomers are distinguishable from those of structural isomers in that the former are much more sensitive than the latter to any physical or chemical influence that may change the entropy of the reaction. This relation must be constantly kept in mind in stereochemical investigations; indeed, there is no exaggeration in the statement that the present confused condition of the theory is, in no small measure, due to the purely mechanical conceptions by which stereomeric processes are judged.[4] For illustration, two cases will be considered: Cinnamic acid dibromide (201°), when decomposed by alcoholic potash, yields a mixture of α-bromcinnamic and α-bromallocinnamic acids, in the proportion of about one part to seven; but if the ethyl ester corresponding to this dibrom acid is treated in the same manner the above relation in the quantities of the α-bromcinnamic acids is reversed, being changed to about ten parts to seven.[1] The primary action of potash on cinnamic acid dibromide is to form the corresponding salt; this is followed by the elimination of hydrobromic acid to form α-bromcinnamate. If we assume that there is only a slight intramolecular obstacle to the development of the maximum entropy in the elimination process, it should proceed largely with the formation of the salt of α-bromallocinnamic acid, as this acid is more acidic than its stereomer and should be better neutralized by the strongly positive potassium.[2] Sudborough and Thompson[3] have shown that the primary action of alcoholic potash on the ester dibromide is the abstraction of hydrobromic acid before saponification occurs. Starting, therefore, with the ethyl ester instead of the acid, and assuming, as with the potassium salt, that there is no especial hindrance to the development of maximum entropy in the elimination process, we have this problem: which of the two α-bromcinnamic acids will better neutralize an ethyl radical? In the fact that ethyl requires for neutralization a less acidic acid than potassium, we have the explanation why the ester of the less acidic α-bromcinnamic acid is formed in greater proportion to that of α-allobromcinnamic acid[4] than in the above case of the potassium derivatives.

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[1] Kahlbaum: Ber. d. chem. Ges., **12**, 2339.

[2] Hydrochloric acid and phenylpropiolic acid unite to form two β-chlorcinnamic acids (Michael and Pendleton: J. prakt. Chem. **40**, 65), but their behavior on reduction has not been examined. How sensitive such reactions may be is shown by the fact that hydriodic acid also forms two β-iodocinnamic acids, but they are both reducible to cinnamic acid (Michael and Whitehorne: Ber. d. chem. Ges., **34**, 3660).

[3] Erlenmeyer: Ann. Chem. (Liebig), **283**, 23.

[4] Since optical isomerism is not strictly speaking a chemical phenomenon, but a mechanical result, it has been possible to correlate facts and theory very successfully by means of the mechanical Le Bel-van't Hoff theory. See Ber. d. chem. Ges., **34**, 3647; J. prakt. Chem., N. F., **75**, 117.

Before considering the stereomeric relations between maleic and fumaric acids and their addition products, I wish to discuss briefly a recent attempt of Pfeiffer[1] to modify the van't Hoff hypothesis in such a manner as to reconcile facts and theory. When it was proved[2] that the higher melting fumaroid modification of the stereomeric halogen-succinic acids loses halhydric acid or halogen more readily than the lower melting maleinoid stereomer, and that fumaric derivatives are direct products of the addition of these reagents to acetylenedicarboxylic acid, attention[3] was directed to the fact that Wislicenus and other chemists had based various configurations on the false assumption that additions always proceed with formation of *cis* products, and that eliminations take place more easily with these than with the trans stereomers.

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[1] Sudborough and Thompson: J. Chem. Soc., **83**, 676 (1903). These chemists have overlooked the fact that this reversal in the relative amounts of the α-brom acids, when the ester is used, was first noticed by me in 1887 (THIS JOURNAL, **9**, 280). At the same time, it was proved that the same relation appears when α,β-dibrom- and α,β-dichlorbutyric acids and their ethyl esters are treated with alkalis.

[2] An application of the law of chemical neutralization; see Ber. d. chem. Ges., **38**, 23.

[3] J. Chem. Soc., **83**, 678.

[4] This relationship explains why phenylpropiolic acid may be obtained purer and more readily from the ester than from free cinnamic acid dibromide, since α-bromcinnamic acid loses hydrobromic acid more easily than the α-allo acid. If a mixture of these two acids is available for the preparation of phenylpropiolic acid, it is obviously advantageous to convert the latter into the former acid by heating, as Whitehorne and myself (Ber. d. chem. Ges., **34**, 3648) have already recommended. Our method consisted in melting the mixture in a platinum crucible and then, *without removing the flame*, keeping it in a molten condition for about a minute. Unfortunately, we did not state explicitly that the flame was not removed, and Sudborough and Thompson (J. Chem. Soc., **83**, 686) have therefore assumed that the mixture was heated no higher than its melting point; they prove that the amount converted is slight at that temperature.

It was also stated that if chemists still deemed it desirable to employ configurations, it would be necessary to accept the power to form anhydrides as the test in classifying the unsaturated dibasic acids, and the configurations hitherto assigned to all other stereomers would have to be reversed. The above results have led to the classing of additions and eliminations as *trans* as well as *cis* processes; but, accepting the van't Hoff configuration for acetylenedicarboxylic acid and basing those of the stereomeric dibasic unsaturated acids on the property of anhydride formation, these terms convey a false impression, since such *trans* reactions can take place only when accompanied by intramolecular rearrangements. Pfeiffer assumes that all additions and eliminations with halogen and halhydric acid are *trans*, and that the carboxyl groups in acetylenedicarboxylic acid are in a *trans* position to each other. This fundamental assumption, that additions and eliminations are *trans* processes, was considered by the writer[4] in 1889, when attention was called to the fact that in this way certain reactions which stand in contradiction to Wislicenus's views, and *vice versa*, could be explained. In connecting facts with theory Pfeiffer's ideas are far inferior to those of van't Hoff. Thus, according to van't Hoff's views, the existence of but one acetylenedicarboxylic acid is explained, while, according to Pfeiffer's hypothesis, there is no reason why a maleinoid as well as a fumaroid modification of this acid should not exist, and the remarkable acidity[1] of the acid is hardly compatible with the assumption that the mutual relations of the carboxyl groups in it are comparable to those in the relatively weak fumaric (K: 0.093) and not to those in maleic acid (K: 1.17). Indeed, Pfeiffer appears to have overlooked the important relationship between acidity and the configurations of stereomeric acids. Thus, although he accepts the van't Hoff configurations for maleic and fumaric acids, which explain the greater acidity of maleic acid, yet in his configurations for the crotonic acids and their α-chlor derivatives, methyl and carboxyl are in the *cis* position for the stronger acid. The contradiction between his assumption for monobasic and dibasic acids is obvious.

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[1] Z. physik. Chem., **48**, 40 (1904).

[2] Michael: J. prakt. Chem., N. F., **52**, 291 (1895).

[3] *Ibid.*, **52**, 290 (1895).

[4] *Ibid.*, **38**, 349.

Moreover, Pfeiffer has not considered the fact that the ease of elimination in a *trans* or *cis* position is only a proportionate relation, and that with some substances it takes place quite readily when, in his own configurations, the eliminated parts are in the *cis* position. Indeed, with saturated stereomers there seems to be little or no difference between them in this respect.[2] Further, in many reactions it has been conclusively proved that there is formed simultaneously in the addition process a mixture of stereomers whose relative proportions depend on conditions absolutely incompatible with any mechanical conceptions of the processes.[3]

It is known that maleic acid contains more energy and has a greater acidity constant than fumaric acid; also, in respect to the latter factor, that racemic has a greater value than mesotartaric acid. Fortunately, the constants K for the acid sodium salts of maleic and fumaric acids have been ascertained, with the result that although fumaric has a much smaller constant than maleic acid, in the case of the acid salts this relation is reversed, the fumarate having a greater value than the maleinate.[1] From these results it would appear that in the formation of these acid salts the energy relations existing in the acids undergo a reversal, and as it is unlikely that the formation of the neutral from the acid salts is accompanied by another reversal, these data indicate that sodium fumarate contains more energy than sodium maleinate. Starting from this point of view, we should expect that the addition of hydroxyl to sodium fumarate would give the sodium salt of that modification of tartaric acid which has the greater acidity constant, and that from the maleinate we should obtain the salt of the form possessing the lower constant. This is indeed the case, as Kekulé and Anschütz[2] obtained the salt of racemic acid (K : 0.097) from the fumarate and that of mesotartaric acid (K : 0.060) from the maleinate.

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[1] Acetylenedicarboxylic acid is almost as strong as sulphuric acid (Ostwald: Z. physik. Chem., **3**, 380).

[2] Michael and Mighill: Ber. d. chem. Ges., **34**, 4221.

[3] Straus (Ann. Chem. (Liebig), **342**, 211) has mentioned a number of specific cases showing the inadequacy of Pfeiffer's views. Their number could easily be enlarged, but it seems hardly necessary.

Perkin and Duppa,[3] and also Kekulé,[4] obtained, by heating the silver salt of dibromsuccinic acid with water, a tartaric acid which according to Pasteur[5] was racemic acid, but which Jungfleisch[6] showed subsequently to consist of a mixture of racemic and mesotartaric acids. Later, Demuth and Meyer[7] made an analogous experiment with silver isodibromsuccinate, obtaining in this way racemic acid almost quantitatively. The conversion of the stereomeric dibrom- into dihydroxysuccinic acids by boiling with water has been minutely studied by Lossen and Riebensahm,[8] who found that a mixture of racemic and mesotartaric acids is formed in each case, but that dibromsuccinic acid gives principally mesotartaric acid and the isodibrom acid mainly racemic acid. From these results, it appears that fumaric and mesotartaric acids, and maleic and racemic acids, are very closely connected chemically. Werner[9] explains the evident contradiction between this conclusion and that based on the results obtained by direct oxidation of the salts by assuming that when bromine is added to maleic and fumaric acids a *trans* addition takes place; with hydroxyl, on the contrary, the addition is *cis*.[1] There is, however, no reason why the proportionate relations in the acidity constants for maleic and fumaric acids should undergo a relative change in their conversion, first, into their dibrom addition products, and afterwards, through the action of water, into dihydroxysuccinic acids. Since racemic has a greater acidity constant than mesotartaric acid, the fact that maleic acid, through its dibromide, gives racemic acid agrees with the energy relations. An interesting confirmation that this is the true relationship may be found in an investigation by Walden[2] on the influence that stereomeric acids have on the rotatory power of their *l*-amyl esters. He found that the fumaric and mesaconic esters show a greater molecular rotatory power than the maleic and citraconic esters; also, that this is true for mesotartaric as compared with racemic amyl ester. These results obviously connect maleic and racemic esters; but, under the impression that fumaric and racemic esters are chemically related, Walden[3] calls attention to the discrepancy which he supposes exists between the stereomeric conclusions derived from the investigations of these acids by a chemical and by a physical method.

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[1] Trevor: Z. physik. Chem., **10**, 350; Smith: *Ibid.*, **25**, 242. See also Ostwald: *Ibid.* **9**, 558.

[2] Ber. d. chem. Ges., **13**, 2150; **14**, 713.

[3] J. Chem. Soc., **13**, 102.

[4] Ann. Chem. (Liebig), **117**, 120.

[5] Ann. Chim. Phys., [3], **61**, 484.

[6] Bull. Soc. Chim., [2], **19**, 194.

[7] Ber. d. chem. Ges., **21**, 268.

[8] Ann. Chem. (Liebig), **292**, 295; also, Lossen and Reisch: *Ibid.*, **300**, 5.

[9] Lehrb. d. Stereochemie, p. 226; also p. 204.

Twenty years of ardent stereochemical investigation has led to a considerable increase in the number of compounds that, sometimes rightly and sometimes wrongly,[4] have been classified as belonging to the category of stereomers, and a number of empirical laws in regard to the relations between the physical and chemical properties of such substances have been formulated.

Fortunately in recent years there has been a slow awakening; the belief that the intramolecular relations of the atoms in stereomers can be ascertained by mechanical speculations, and that the intricate chemical relations of such bodies can ever be correlated to a mechanical system is being gradually abandoned.[1]

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[1] Since *trans* additions must in these cases be accompanied by a shifting in the position occupied by carboxyl or hydrogen, and as there is no apparent reason for such complicated changes, such assumptions are of very doubtful value.

[2] Z. physik. Chem., **20**, 377.

[3] *Ibid.*, **20**, 386.

[4] See Ber. d. chem. Ges., **39**, 209.

One of the chief objects of this paper is to call attention to the intimate connection between the energy relations of stereomeric substances and their chemical behavior ; further, to point out that our surest sources of information on this subject have been systematically neglected, and to urge the absolute necessity, therefore, of such thermochemical and physicochemical investigations of stereomeric bodies as may lead to the development of a consistent theoretical treatment of the subject.

TUFTS COLLEGE, MASS.

THE ADDITION OF HALOGENS TO CINNAMIC ACID AND SOME OF ITS DERIVATIVES.[2]

BY ARTHUR MICHAEL AND HOWARD D. SMITH.

In an experimental investigation, designed to test the validity of the assumptions on which J. Wislicenus had based his methods for determining the configurations of stereomeric substances, it was shown by one of us[3] that the application of his views to unsaturated, stereomeric dibasic acids led to configurations diametrically opposed to those derived from a consideration of the property of forming anhydrides. Thus, if we base the *cis* relationship of the carboxyl groups on the ability of such an acid to form an anhydride, we must classify bromfumaric acid as a *trans* derivative; on the other hand, if we start from the equally valid argument that with a *cis* relationship existing between the hydrogen and bromine a more ready elimination of bromhydric acid takes place than when these elements are in a *trans* position, we must denote the same acid by a *cis* configuration. If we accept the assumption in regard to anhydride formation as correct, we are forced to the conclusion that additions and eliminations do not take place as *cis*, but mainly as *trans* processes; and, starting from this idea as a means of classifying stereomeric unsaturated compounds, all configurations which Wislicenus and his supporters had previously assigned to unsaturated substances have to be reversed,[1] excepting, of course, those of the unsaturated dibasic acids which are based on the property of forming anhydrides. While this fundamental contradiction between the methods for determining configurations obviously made all speculations on the intramolecular arrangement of atoms in stereomers of very doubtful value, yet the application of the addition-elimination principle[2] to the classification of stereomeric substances provided at least a means of expressing in general laws the relationship between the physical and chemical properties of such stereomers.[3] Thus, of two unsaturated stereomeric acids, that denoted by the unstable maleinoid condition should melt at a lower temperature and be more soluble than the other form. The same relationship appears also in the halogen derivatives of these acids. The higher melting of these stereomers is the one which is formed by the addition of halhydric acid or halogen from the corresponding acetylenecarboxylic acid, and it, in turn, also gives up the addenda more easily than the lower melting, maleinoid acid in re-forming the mother substance.

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[1] See J. prakt. Chem., N. F., **75**, 117.

[2] This research is not completed, but as Herz and Mylius (Ber. d. chem Ges., **39**, 3816) and Sudborough and Thomas (P. Chem. Soc., **22**, 318) have recently published work bearing on the same subject, it was thought advisable to publish our results.

[3] Michael: J. prakt. Chem., N. F., **52**, 289.

Until 1895, these generalizations were also applicable to the stereomeric cinnamic acids and their derivatives, but in that year, Liebermann and Finkenbeiner[4] made the important observation that when chlorine is added to cinnamic acid in the dark a cinnamic acid dichloride melting at 86°, instead of the stereomeric product melting at 168°,[5] is formed. Judging from this result, it would seem as if the higher melting dichloride were not the primary addition product of cinnamic, but of allocinnamic, acid. This view is apparently confirmed by the fact that with the same conditions under which cinnamic acid gives the lower melting dichloride quantitatively, allocinnamic acid yields mainly the higher melting stereomer.[1]

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[1] Michael: J. prakt. Chem., N. F., **52**, 359.

[2] Werner (Lehr. der Stereochemie, p. 210) remarks that the law governing the relations between the formation of stereomeric addition products and their reconversion into the original substances (Michael: Ber. d. chem. Ges., **34**, 4215) may be considered probable, as it harmonizes with the conception that the formation of stable proceeds through those of unstable modifications. The comparison is untenable, for in structural addition reactions the actual product is always the more stable of the possible isomers, *under the conditions of its formation*, and the same relationship exists in stereomeric additions. Werner has overlooked the fact that the experimental conditions in the elimination are entirely different from those in the addition experiments. (A. M.)

[3] J. prakt. Chem., **52**, 344.

[4] Ber. d. chem. Ges., **28**, 2235.

[5] Erlenmeyer: *Ibid.*, **14**, 1867.

In apparent contradiction to this view are the observations that both allocinnamic acid and its methyl ester, treated in the dark with an excess of bromine, give 30–40 per cent of a lower melting dibromide along with the ordinary form, and that these lower melting products are not obtained from cinnamic acid and its ester under the same experimental conditions.[2]

An interesting contribution to this subject was made by Plöchl and Mayer,[3] who showed that the phenylglyceric acid (141°) formed by the mild oxidation of cinnamic acid[4] could not be resolved into optically active components; further, a stereomer (120°) obtained from the higher melting cinnamic dibromide[5] was shown in this way to possess a racemic structure. A comparison of these results with those obtained in similar experiments with maleic and fumaric acids[6] led these chemists to the conclusion that cinnamic acid is not chemically related to fumaric, but to maleic, acid. Several years later,[7] it was shown that by using carbon tetrachloride as a solvent and adding the bromine to cinnamic ethyl ester in the dark, over 50 per cent, and from methyl cinnamate about 35 per cent, of allodibromides, along with the higher melting dibromides, could be obtained. Furthermore, the methyl ester allodibromide formed in this way is identical with the product which Liebermann[8] had previously obtained (mixed with 50–60 per cent of the stereomer) from methyl allocinnamate, thus proving definitely that the addition of bromine to cinnamic and allocinnamic derivatives, under certain conditions, may give the same allodibromide. Allocinnamic acid was also oxidized with potassium permanganate and the lower melting racemic phenylglyceric acid (120°) obtained in this way.

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[1] Liebermann: Ber. d. chem. Ges., **27**, 2040.

[2] *Ibid.*, **24**, 1108; **27**, 2038.

[3] *Ibid.*, **30**, 1600.

[4] Fittig and Ruer: Ann. Chem. (Liebig), **268**, 27.

[5] Anschütz and Kinnicutt: Ber. d. chem. Ges., **12**, 537.

[6] Kekulé and Anschütz: *Ibid.*, **14**, 713.

[7] Michael and Whitehorne: *Ibid.*, **34**, 3660.

[8] Ber. d. chem. Ges., **24**, 1107.

The experiments on the formation of ethyl cinnamate allodibromide from ethyl cinnamate and bromine were repeated by Sudborough and Thompson,[1] but for some unknown reason these chemists were unable to observe the formation of more than a trace of the allodibromide. This led us to repeat the experiments of Michael and Whitehorne, and our results are practically identical with theirs. It was emphasized in the former paper[2] that the proportion of allodibromide to dibromide formed in these reactions is dependent on very subtle conditions; although we have made a number of new experiments to enable us to define these more precisely than before, we have not succeeded in accomplishing our object. It may be stated, however, that in thirty experiments, using carbon tetrachloride as a solvent and adding the bromine in the dark, we always obtained some allodibromide, no matter in what other respect the conditions of the experiment were changed; indeed, in some of the experiments almost 50 per cent of the mixture consisted of this product.

Liebermann and Finkenbeiner[3] prepared cinnamic acid allodichloride by passing an excess of chlorine into a mixture of cinnamic acid and carbon tetrachloride, the necessary precautions for a successful result being (*a*) that the mixture should be carefully cooled with ice, (*b*) kept in the dark during the operation, and (*c*) then allowed to stand without shaking 8–14 days in an ice chest. The solution obtained in this way, after evaporation of the solvent in a vacuum desiccator and subsequent standing for 3–4 days in a cool, dark place, yielded the allodichloride as an oil. This product could be obtained in crystalline form only by a tedious process of purification through the cinchonidine salt, although the oil could be made to solidify by the addition of a small amount of the crystalline acid. Judging from the results of our experiments, it does not seem at all necessary to follow these laborious directions. We find that when a cold mixture of cinnamic acid and a solution of chlorine in carbon tetrachloride is exposed to strong, direct sunlight, mainly the higher melting dichloride is formed, although a relatively small amount of the stereomer is also obtained. The proportion of the latter to the former acid is very considerably increased, however, if rays of sunlight are first passed through solutions capable of absorbing the violet end of the spectrum. This result indicates that the conversion of the allodichloride into the ordinary dichloride may be attributed to absorption of energy from the actinic light rays.[1] Furthermore, this conversion is largely dependent on the intensity of the white light, for we noticed that the addition proceeds with the formation of a considerable quantity of allodichloride if the operation is carried out in diffused light. According to our observations all the other precautions so scrupulously observed by Liebermann and Finkenbeiner are immaterial and may be disregarded.

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[1] J. Chem. Soc., **83**, 671 (1903).

[2] Ber. d. chem. Ges., **34**, 3662.

[3] *Ibid.*, **28**, 2236.

By using the methyl ester instead of cinnamic acid very similar results were obtained: in sunlight, practically only the high melting ester dichloride (101°) is formed; in diffused light, a mixture of this substance with the oily allodichloride; and in the dark, practically nothing except the latter substance.[2] Cinnamyl chloride gave analogous results: in the dark, an oily dichloride, corresponding to cinnamic acid allodichloride; in bright sunlight, a solid addition product which yielded cinnamic acid dichloride when decomposed by water.

Cinnamic acid, although in its physical properties, energy relations, and stability towards all chemical reagents that do not change its chemical nature, so distinctively a fumaroid derivative, yields, notwithstanding, with chlorine the unstable allodichloride as the primary addition product. The maleinoid allocinnamic acid, on the other hand, gives the more stable higher melting dichloride, although the comparatively small amount of oily dichloride formed along with the high melting body may, indeed, prove to be the lower melting dichloride.[1] Such a result is best explained, however, on the assumption that the latter is formed indirectly from some cinnamic acid previously stereomerized by the action of the halogen on the allocinnamic acid. The results obtained by the addition of bromine to the stereomeric cinnamic acids are also, as yet, best explained when considered from the same point of view.

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[1] See explanation in the preceding paper.

[2] Compare Liebermann: Ber. d. chem. Ges., **28**, 2239.

In the cinnamic series, the conditions governing addition reactions vary with the nature of the additive reagent to an extent quite unknown in other groups of unsaturated acids. Under conditions where the allodichloride is formed quantitatively from cinnamic acid, allodibromide is obtained in a comparatively small amount,[2] and in the action of bromine on cinnamic ester the yield of allodibromide depends to a considerable extent on the solvent used.

In the preceding paper, one of us has endeavored to show that a reversal in the energy relations between maleic and fumaric acids takes place when these acids are converted into salts; under such conditions maleic acid is related to racemic and not to mesotartaric acid. As far as we can judge at present, such a reversal does not occur when the stereomeric monobasic cinnamic acids are converted into salts; this view is confirmed by the facts that mesophenylglyceric acid is formed in the oxidation of potassium cinnamate, and that the higher melting cinnamic acid dibromide, which is not the primary but the secondary product of the addition, has been converted into racemic phenylglyceric acid. Sudborough and Thompson[3] have advanced, as an argument against the conclusion that the high melting ethyl cinnamate dibromide (76°) is not the primary addition product of cinnamic, but of allocinnamic, ester, the fact that in this case the high melting cinnamic acid dibromide should give α-bromcinnamic acid on treatment with alkalis, whereas mainly α-bromallocinnamic acid is formed. This behavior cannot be considered a valid objection, since it is based on analogy and on views which seek to explain such chemical processes from a mechanical standpoint. A similar argument would make the primary formation of the unstable allodichloride from the stable cinnamic acid an impossibility, because the addition of chlorine to fumaric acid yields a fumaroid product. Indeed, in the same paper,[1] Sudborough and Thompson show how little value is to be placed on such speculations about stereomeric relations, since they prove that by decomposing the ethyl ester instead of the acid, the relative proportions are reversed, the reaction proceeding with the formation of considerably more α-bromcinnamic than of α-bromallocinnamic acid.[2]

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[1] Several experiments were made on the addition of chlorine to allocinnamic acid and under different conditions we succeeded in obtaining a greater proportion of an oily dichloride than Liebermann. It seems doubtful if the product is identical with that obtained from cinnamic acid, as it is less soluble in petroleum ether. These experiments will be continued.

[2] I intend to make further experiments on the addition of bromine to cinnamic acid, with special reference to the conditions that Liebermann employed when he succeeded in obtaining some allodibromide from allocinnamic acid. (A.M.)

[3] J. Chem. Soc., **83**, 678.

Addition of Chlorine to Cinnamic Acid.

Instead of suspending cinnamic acid in carbon tetrachloride and then passing into the mixture rather more than the theoretical amount of chlorine,[3] the finely pulverized acid was added to a solution of chlorine in the same solvent.[4] The latter was saturated at ordinary temperature, and was of known strength, containing somewhat more halogen than required by the theory.

I. Five grams of cinnamic acid were added to the chlorine solution, contained in a brown glass bottle. This was packed in a tin can, which was then covered and placed in an ice chest. After standing one day, the contents of the bottle were examined in yellow light and found still to contain a considerable amount of undissolved cinnamic acid, which, however, in the course of another day, had almost all disappeared. After standing four days a clear solution had formed, which contained some free chlorine and a little hydrochloric acid; moreover, a very small amount of the crystalline higher melting dichloride had separated out. After distilling off the solvent and exhausting in a vacuum to constant weight, a thick oily residue, 7.1

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[1] p. 676.

[2] Explained in the preceding paper.

[3] Liebermann and Finkenbeiner: Ber. d. chem. Ges., **28**, 2236.

[4] Michael: J. prakt. Chem., N. F., **46**, 225.

grams (theory 7.49), of the addition product was obtained. Part of the oil was then dissolved in petroleum ether (60°–70°), and as the allodichloride did not separate out, almost all the solvent was driven off by heating the solution, and the residue placed in the ice chest. After standing three days it had partially solidified, yet even after a month there still remained a small amount of oil mixed with the crystals. The oil which had not been treated with petroleum ether also partially solidified on standing, but this took place more slowly. The product, after being dried on a porous plate, melted at 80–84° and was almost pure allodichloride (84°–86°).

II. The experiment was repeated, using a brown glass bottle, which excluded the violet rays, and placing it in an ordinary glass beaker containing ice water, in direct sunlight. The addition proceeded more slowly than when the mixture was in a colorless glass bottle; after three hours' exposure to sunlight there still remained considerable unchanged cinnamic acid. During the night the addition was completed, and a small quantity of the high melting dichloride separated out. The oily residue, after removal of the solvent, gradually crystallized, but the product apparently contained some of the higher melting dichloride, as it melted from 75°–100°.

III. Number II. was repeated, except that the brown glass bottle was placed in the focus of a mirror, and exposed to strong sunlight during two days. The addition took place much more rapidly, and some of the high melting dichloride had formed after exposure for several hours. At the end of the experiment more than two-thirds of the addition product consisted of the high melting dichloride.

IV. Like II., but the mixture was placed in a white glass bottle and the day was cloudy. On exposure to light the mixture heated perceptibly, and it was then cooled in ice water. After two hours all the halogen had disappeared. The precipitate (5.9 grams) consisted of dichloride, and the filtrate yielded 0.9 gram oil. The oil was a mixture of dichloride and allodichloride.

V. Repeated IV. on a very cloudy day, cooling off at once in ice water. The chlorine had disappeared after 3–4 hours' exposure. Obtained 3.8 grams of dichloride and 3.2 grams of allodichloride from the solvent.

VI. Repeated IV., using an ordinary bottle, and leaving the mixture without external cooling in the dark part of a room and out of the direct line of light from a window. After standing for a day all the cinnamic acid went into solution, and in the course of another day a very small amount of dichloride separated out. The solution gave almost the theoretical quantity of an oil, about three-fourths of which gradually solidified. It consisted of allodichloride. This experiment was repeated several times with the same result.

VII. Repeated VI., placing the bottle in diffused light, but in the rear part of the room. During the day it was exposed for several hours to direct sunlight. We obtained 2.5 grams of chloride and 5.6 grams of allodichloride.

VIII. Two grams of cinnamic acid and a slight excess of chlorine in tetrachloride solution were brought, in yellow light, into a colorless glass bottle, which was then placed in a box that admitted only light passing through a prism. This prism contained a 2 per cent solution of potassium bichromate, and cut off all rays of light excepting red, yellow, orange, and green. The box was so placed in bright sunlight that the contents of the bottle were exposed to the light passing through the prism. The addition took place very much more slowly than in white light. This experiment gave 1.7 grams dichloride and 1.05 grams allodichloride, and on repetition 1.8 grams of the former and 1.0 grams of the latter product. At the same time, an experiment was made in which the mixture was exposed to ordinary sunlight; only the dichloride was obtained as a result.

IX. The preceding experiment was repeated, using a 1 per cent solution of iodine in alcohol in the prism. The addition took place very much more slowly than in white light, and a mixture of the stereomeric dichlorides was obtained.

The oily addition product formed in the above experiments contained a small amount of the higher melting dichloride. The greater part of this product was removed by extracting the mixture with a very small amount of benzene and, after allowing it to stand for a day in the ice chest, filtering off the dichloride that separated out. The oil remaining after evaporation of the solvent gradually crystallized, and on drying on a porous plate was found to be almost pure allodichloride.

Addition of Chlorine to Methyl Cinnamate.

I. The ester was added to a solution of chlorine (slight excess) in carbon tetrachloride in an ordinary glass bottle, the mixture cooled off in ice water, and then placed in direct sunlight. The addition proceeded faster than with cinnamic acid, and a colorless solution was obtained in about ten minutes. On further standing in sunlight, crystals gradually separated out. These crystals were identical with cinnamic methyl ester dichloride[1] (101°), a further quantity of which was obtained on evaporation of the solvent. Only a trace of the oily addition product was present.

II. The result of the above experiment seemed to indicate that the primary addition product was allodichloride, which, by exposure to sunlight, had been converted into dichloride. The experiment was repeated, but as soon as the discoloration of the solution (eight minutes) was complete, the bottle was placed in an ice chest. Under these conditions also, the separation of the dichloride took place gradually, and its slow separation from the solution is therefore probably due to supersaturation. Only a small amount of the oily product was formed.

III. The mixture, in a brown glass bottle, was kept in an ice chest. The addition proceeded slowly; after two days there was still free chlorine, but in another two days this had disappeared. No crystals separated from the solution on standing. The solvent was distilled off under reduced pressure, and the residue placed in a vacuum desiccator in an ice chest. After three days, some crystals were deposited; these were separated from the oil by addition of carbon disulphide and filtration. From 2 grams methyl ester, only 0.2 gram of the dichloride was obtained; the oil did not solidify on long standing, and was identical with the methyl ester allodichloride prepared by Liebermann[2] from cinnamic acid allodichloride.[3]

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[1] Finkenbeiner: Ber. d. chem. Ges., **27**, 890.

[2] Ber. d. chem. Ges., **28**, 2239.

[3] Liebermann (*Ibid.*, p. 2242) obtained mainly dichloride by the addition of chlorine to allocinnamic methyl ester. Unfortunately, it is not stated whether the experiment was done in the dark.

Addition of Chlorine to Cinnamyl Chloride.

Cinnamyl chloride was prepared by the action of phosphorus pentachloride on cinnamic acid; the product of the reaction was fractionated in a vacuum.[1] The chloride boils at 136°–137° under 15 mm., melts at 35°–36°, and is soluble in carbon tetrachloride and petroleum ether.

I. A solution of 5 grams chloride and the theoretical amount of chlorine in carbon tetrachloride was brought into a glass bottle, cooled in ice water, and exposed to direct sunlight. The addition proceeded quickly; in half an hour free chlorine was present only in traces. After distilling off the solvent a thick yellowish oil remained; this solidified almost entirely, on standing, to a crystalline mass. It was dried on a porous plate, and then crystallized from petroleum ether (45°). The addition product is very soluble in carbon disulphide, acetone, acetic acid, chloroform, benzene, and hot petroleum ether, moderately in cold ether, and less in cold petroleum ether. It crystallizes from the latter in prismatic needles with rounded ends, melts at 54°–55°, and is quite stable towards water; a mixture required ten hours' shaking for complete decomposition, and then gave pure cinnamic acid dichloride. Analysis:

0.1295 gram substance gave 0.2337 gram AgCl.

	Calculated for $C_6H_5.CHCl.CHCl.COCl$.	Found.
Cl	44.7	44.6

The chloride is very stable towards chlorine; in a second experiment a slight excess of chlorine was used, and the solution was not decolorized after several hours' exposure to sunlight.

II. The above experiment was repeated, using a brown bottle, and keeping the mixture in an ice chest. The addition proceeded slowly and was not completed before two days. Evaporation of the solvent yielded the theoretical amount of a yellowish oil, which could not be made to crystallize. The oil was readily soluble in carbon tetrachloride and petroleum ether, and as it gave, on decomposition with water, cinnamic acid allodichloride and dichloride, it undoubtedly consisted of a mixture of the chlorides of these stereomeric acids.

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[1] Claisen and Antweiler: Ber. d. chem. Ges., **13**, 2124.

Addition of Bromine to Ethyl Cinnamate.

The following experiments were carried out in the dark, with carbon tetrachloride as a solvent. Slightly more (0.59 gram) than the theoretical amount of bromine was used. According to the previous work on this subject, these are conditions favorable for the formation of allodibromide. The variations in the experiments consisted in adding the halogen either in portions, or the full amount, to the solution of the ester (5 grams), which was kept at room temperature, or cooled off in ice water; and in the length of time the mixtures stood before they were worked up. During the experiments the mixtures were carefully excluded from exposure to light, and kept in a cool place.

I., II., and III. The mixtures were cooled in ice water, and after the bromine had been added in three portions, at intervals several hours apart, were allowed to stand a day. Yields: 14.6, 27.5, and 51.0 per cent of allodibromide.

IV., V., VI., VII., VIII., IX., and X. The halogen was added at once to the cooled solutions of ester in tetrachloride. IV. and VI. stood one day; V. and IX., three days; VII., five days; and VIII. and X., one week. The yield of oily dibromide was 14.4, 23.3, 25.4, 26.9, 31.1, 32.0, and 34.4 per cent.

XI., XII., and XIII. The solutions of ester were kept at room temperature and the halogen added in portions. XI. stood one day, and XII. and XIII., one week. Yields: 32.5, 47.3, and 49.4 per cent of oil.

XIV., XV., XVI., and XVII. As in the preceding experiments, the halogen was added only in one portion. The first three experiments stood a day, the last a week. Yields: 17.4, 28.4, 30.0, and 47.2 per cent of oil.

In these experiments, the series giving the greatest yield of allodibromide was that in which the solution was not cooled and where the halogen was added in portions; we wish to emphasize, however, that the yield of this compound depends on such subtle conditions that we do not consider our experiments as more than suggestive for future investigation. In every experiment some hydrobromic acid was obtained, but in varying amount; we could not find any connection between the relative amounts of the mineral acid and the allodibromide formed in the additions.

On standing in an ice chest, the oily dibromide deposited a small amount of the high melting dibromide, and then gradually solidified, largely to the allo product. When the crystals of the higher, with some of the lower, melting dibromide were removed from the oil, and the solid product subsequently formed was dried on a porous plate and washed with low boiling petroleum ether, it melted at 33°–35°, although it began to soften at 28°. In an earlier investigation,[1] a product melting at 28°–30° was obtained by partially melting the impure allodibromide, separating the liquid from the solid part, and repeating this operation a number of times. We endeavored to purify the allodibromide by crystallization from light petroleum ether (38°–45°), and in this way obtained a product melting at 28°–32°. It is very improbable, however, that absolutely pure allodibromide can be obtained by either of these methods.

Addition of Bromine to Methyl Cinnamate.

Michael and Whitehorne have shown that methyl cinnamate allobromide is formed in considerable proportion to the dibromide when the addition is carried out in the dark, but in view of the negative results of Sudborough and Thompson with the ethyl ester it was thought desirable to repeat this experiment.

Five grams of methyl ester were dissolved in carbon tetrachloride, the solution placed in a brown bottle, a slight excess of bromine added, and the mixture put in a closed tin box. After standing several days in an ice chest, the crystals of dibromide (116°–117°) which had separated out were removed by filtration. The filtrate, on evaporation in a vacuum, left an oil which solidified on standing. To separate the stereomeric dibromides, this product was crystallized from alcohol; the filtrate gave 1.7 grams of the allodibromide, melting at 54°–55°. A similar experiment, but using petroleum ether instead of carbon tetrachloride, gave a very much smaller yield of the allodibromide.

TUFTS COLLEGE, MASS.

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[1] Michael and Whitehorne: Ber. d. chem. Ges., **34**, 3661.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

STUDIES IN CATALYSIS. I. THE CATALYSIS OF ESTERS AND OF IMIDOESTERS BY ACIDS.[1]

By Julius Stieglitz.

When an acid ester like methyl acetate is treated with water it is partially saponified, and a condition of equilibrium is ultimately established, according to the familiar equation,

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOH + CH_3OH.$$

As is well known, the saponification proceeds exceedingly slowly under these conditions, but if an acid is added to the mixture, the reaction is accelerated in direct proportion to the concentration of the hydrogen ions used, and the ultimate condition of equilibrium is reached very much more rapidly. This effect of the acid or of the hydrogen ions belongs to that most interesting class of actions known as catalytic. While certain limitations and laws of catalytic action are well understood, one of the fundamental features of such actions is still largely shrouded in mystery, and that is the question as to how the catalyzer does its work. We know *what* it does, but comparatively little has been done experimentally to prove rigorously *how* it does it.

The common catalytic agents may well be divided into two or, perhaps better, three classes: (1) Purely chemical agents, such as the acids and the alkalis, acting in homogeneous mixtures; (2) Physical agents, such as finely divided platinum, colloidal metals, light rays, and the like; (3) agents which may perhaps act simultaneously both chemically and physically. Possibly some of the enzymes act in this way.

It is intended to discuss here only reactions belonging to the first class of catalytic actions, particularly the action of acids on the catalysis of acid esters. It is thought, however, that the conclusions arrived at are, in principle, equally applicable to the other classes of catalysis. It seems best not to attempt to give a rigorous definition of catalysis at the outset; the definition, as has often been the case, might be drawn too narrowly and thus hamper the free study of the thing itself.[1] In the case of the catalysis of the esters, we are certain of three main facts which have been proved experimentally: the action is accelerated in proportion to the concentration of the hydrogen ions present; the acid appears to remain unchanged throughout the course of the action, to remain uncombined with any of the compounds involved; and the ultimate condition of equilibrium is not measurably changed by the presence of the acid, that is, the velocities of the two reversed reactions, saponification and esterification, must be affected in a like manner and to a like degree by the presence of the acid. Whether all or any of the three characteristic features of this action may properly be considered characteristic of all catalytic actions, as is sometimes claimed, is open to question. This will become apparent below.[2]

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[1] A report of the leading ideas and facts of this paper was made by the author in his address on "The Relations of Organic Chemistry to Other Sciences" before the section on Organic Chemistrv of the International Congress of Arts and Science at St. Louis, September, 1904. See **4**, 276 of the Report.

In trying to imagine how an acid can affect the decomposition of an ester by water, we are led to recall the most fundamental property of acids, that of combining with bases and oxides to form ionizable salts. In the case under discussion we have, beside the acid, the oxide also, namely, the ester, and so we are led to the idea that an ester like methyl acetate may have basic functions and that salt formation with the acid may be the explanation of the fact of its catalysis. It was clear, at the time this idea was developed,[3] that the basic properties of an ester must be so weak that a quantitative measurement of its affinity constant and of the conditions of equilibrium of its salts could not readily be made by the methods of measurement known. Under the circumstances it was thought best to study the factors involved in a class of very closely related bodies, the imidoesters, with which quantitative measurements of all the factors could actually be carried out. The imidoesters, RC(:NH)OR′, acid esters in which the imide group (:NH) replaces the oxygen atom of the ordinary esters, are markedly basic substances which are very slowly decomposed by water; they form well-defined salts which are very rapidly decomposed by water—the analogy appeared complete for the object of our study. There are minor differences, which will be pointed out in the proper place, but in this fundamental characteristic fact the parallelism is perfect, and the deeper the investigation was carried, the more complete the analogy between the two classes appeared to be.

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[1] Report of the Congress of Arts and Science, St. Louis, 4, 278 (1904).

[2] See end of Part III, p. 47.

[3] The work was started in 1898.

The study of the action of water on the imidoesters and their salts has been carried out with Messrs. I. H. Derby, W. Mc Cracken, and H. I. Schlesinger. In other papers they will present, in detail, the experimental results on a large number of imidoesters; at the present moment it is desired only to present the theoretical discussion of the questions at issue, to give the main results established by experiment, and to draw the necessary conclusions as to the nature of the catalysis of imidoesters and of ordinary esters.[1]

I. The Decomposition of the Imidoesters.

When methyl imidobenzoate is dissolved in water, it is very slowly decomposed, giving almost entirely methyl alcohol and benzonitrile, according to[2]

$$C_6H_5C(NH)OCH_3 \rightarrow C_6H_5CN + CH_3OH \qquad (1).$$

To a minimal extent only, it forms methyl benzoate and ammonia, according to[3]

$$C_6H_5C(NH)OCH_3 + H_2O \rightarrow C_6H_5COOCH_3 + NH_3 \qquad (2).$$

Both reactions are practically nonreversible under the conditions of the experiment. The addition of hydrochloric acid to the solution enormously increases the velocity of the second reaction, and this may become practically the exclusive reaction. The acid forms the hydrochloride with the base, but, as an imidoester is a very weak base, we have, in an aqueous solution of its hydrochloride, partial hydrolysis of the salt, and a condition of equilibrium is established, according to

$$C_6H_5C(NH_2Cl)OCH_3 + H_2O \rightleftarrows C_6H_5C(NH_2OH)OCH_3 + HCl \quad (3).$$

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[1] I wish to take this opportunity to thank my young collaborators for their faithful work and valuable assistance. All the experimental work was carried out by them under my guidance.

[2] See Schlesinger's article.

[3] The experimental proof of this was recently brought out by Miss Edith E. Barnard.

In such a solution it may be the salt or its positive ion thta is undergoing the rapid saponification, it may be the free base, or it may be all indifferently. A quantitative investigation of the relations promised to give a conclusive answer to the question as to just how the acid accelerates so decidedly reaction (2), whether by its mere presence or rigorously by the formation of the salt or its positive ion. It may be stated at once that the experimental results prove conclusively that the reacting substance which gives ammonia and a benzoic ester is, as was expected, only the salt or, rather, *only its positive ion*, and that the accelerating action of the acid is simply due to the formation of *larger reacting masses of the active ion from the scarcely ionized, weak base.*

From the results of Messrs. Derby, McCracken, and Schlesinger it also appears that the decomposition of imidoesters by water under the influence of acids is subject, *like that of the ordinary esters*, to an accelerating "salt-effect," due, most likely,[1] to the effect of the presence of many ions on the *ionization* of *water* which enters into the reaction (equation 2). The material gathered relative to this fact being rather fragmentary, the investigation of this "effect" and of the closely related question of the effect of the presence of nonionized substances has been carried on by Miss Barnard. Her work has shown that again, as in the catalysis of acid esters, nonionized substances have no effect on the velocity of the action between imidoester salts and water, but electrolytes have a decided "salt effect." Later papers will present the results in detail.

It was also found in the work of Mr. Schlesinger that the decomposition into nitrile and alcohol according to reaction (1) is enormously accelerated, proportionately to the concentration of the hydroxyl ions used, by the addition of alkalis. This brought out a further line of analogy between the imidoesters and the acid esters. As will be shown and fully discussed by Schlesinger in a later paper, the accelerating effect of the alkali is considered, by analogy with the proved explanation of the catalytic effect of the acids, to be due to very weak acid properties of the imido-

[1] Euler: Z. physik. Chem., **32**, 348 (1900).

esters (they are amphoteric), the alkali producing an increase in the concentration of the *negative ions*, which form the *reacting mass in the decomposition into nitrile and alcohol* according to equation (1).

From studies of the decomposition of an imidoester in a purely aqueous solution, carried out with Derby and with Schlesinger, it appears that the *nonionized molecules* of the imidoesters also break down to nitrile and alcohol, but with a velocity constant which is exceedingly small as compared with that for the decomposition of the negative ions.

We have, therefore, the following three simultaneous decomposition reactions for an imidoester, each proceeding according to an established velocity constant:

$$\text{(I.)}\quad C_6H_5C(:\overset{+}{N}H_2)OCH_3 + H_2O \longrightarrow C_6H_5COOCH_3 + \overset{+}{N}H_4,$$

$$\text{(II.)}\quad C_6H_5C(:\overset{-}{N})OCH_3 \longrightarrow C_6H_5CN + \overset{-}{O}CH_3,$$

$$\text{(III.)}\quad C_6H_5C(NH)OCH_3 \longrightarrow C_6H_5CN + HOCH_3.$$

The theoretical significance of these results for the question of catalytic action, and their application to the catalysis of ordinary esters, will be discussed in Part III., after the presentation in Part II. of the mathematical treatment of the problem with a condensed summary of some of the experimental results.

II. The Velocity of Decomposition of Imidoesters by Aqueous Acids.

The reaction which is accelerated by the addition of an acid to an imidoester, as explained above, is its decomposition by water into ammonia and an acid ester, according to

$$RC(NH)OR' + H_2O \longrightarrow RCOOR' + NH_3 \qquad (2).$$

A salt is formed which is partially hydrolyzed, according to

$$RC(:NH_2Cl)OR' + H_2O \rightleftarrows RC(NH_2OH)OR' + HCl \quad (3).$$

It was early observed that the salts of the weaker bases, which are more highly hydrolyzed into the free base and the acid, were also most rapidly decomposed according to reaction

(2). In such a solution, then, the substance actually undergoing this decomposition might be the base and salt indifferently, the free base present, or only the salt (its positive ions). These three possibilities are expressed in the equations

$$\frac{dx}{dt} = k_{subst} \times C_{subst} \qquad \text{(I.)},$$

$$\frac{dx}{dt} = k_{base} \times C_{base} \qquad \text{(II.)},$$

$$\frac{dx}{dt} = k_{salt} \times C_{salt} \qquad \text{(III.)},$$

in which C_{subst}, C_{base}, and C_{salt} are functions of x and always represent the concentration of the substance indicated at the moment t.

For the last case, in the presence of considerable amounts of the free base, we would have, rigorously, also the possibility of the rapid decomposition of the salt or its ions, according to equation (2), occurring simultaneously with the very slow decomposition of the nonionized free base according to reaction (1) (p. 31), which might take place at the same rate as it does in the absence of any acid. We would have then

$$\frac{dx}{dt} = k_{salt} \times C_{salt} + k'_{base} \times C_{base} \qquad \text{(III'.)},$$

where k_{salt} is the velocity constant of equation (III.) and k'_{base} is the velocity constant of the transformation of the base into benzonitrile and an alcohol according to (I.), as determined in Part VII.[1] Where the amount of the free base is small, the velocity of its transformation being also exceedingly small, (III.) may be substituted for (III'.) as expressing the course of the mixed reaction.

In order to test these possibilities, it was necessary to determine two things experimentally: first, the actual change x in time t; and, second, the proportion of salt, free base, and acid present at any moment t. The rate of change was determined by simple alkalimetric titration methods which will be described in the reports of my collaborators. In regard to the second point, considering the equilibrium equation (3), we have for the free weak base present

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[1] See a later paper.

$$C_{pos.\ ion} \times C_{OH} = k_{base} \times C_{base} \qquad (4).$$

For dilute solutions at 25°,

$$C_H \times C_{OH} = k_{H_2O} = 1.2 \times 10^{-14} \qquad (5),^1$$

and consequently,

$$\frac{C_{pos.\ ion}}{C_{base} \times C_H} = \frac{k_{base}}{k_{H_2O}} = k_{hydrolysis} \qquad (6).$$

In dilute solutions the salt and the free strong acid, hydrochloric acid, are proportionately and practically completely ionized, while the base is present in nonionized form; so we may write (6)

$$\frac{C_{salt}}{C_{base} \times C_{acid}} = \frac{k_{base}}{k_{H_2O}} = k_{hydrolysis} \qquad (6'),$$

which is Walker's[2] fundamental equation for a hydrolyzed salt solution, as developed by Arrhenius.[3]

$k_{hydrolysis}$ was determined for a number of imidoester salts by conductivity measurements of the solutions. A few of the results follow:

	$k_{hydrolysis}$.
Methyl imidobenzoate	4×10^5
Ethyl "	9.1×10^5
Methyl imido-*m*-nitrobenzoate	5.8×10^4
Ethyl "	8×10^4

With the aid of these constants the equations (I.), (II.), (III.), and (III.') may be solved.

(1) Equation (I.), $\frac{dx}{dt} = k_{subst} \times (C - x)$,

represents a simple reaction of the first order, the whole substance taking part in the action, base and salt indifferently.

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[1] Van't Hoff: "Theoretical and Physical Chemistry," I, 133.

[2] Z. physik. Chem., **4**, 319 (1889).

[3] *Ibid.*, **5**, 19 (1890).

We have, then,

$$k_{subst} = \frac{1}{t_2 - t_1} \text{ log nat } \frac{C - x_1}{C - x_2} \qquad (7).$$

(2) Equation (II.), $\frac{dx}{dt} = k_{base} \times C_{base}$,

represents the velocity of the reaction as being proportionate only to the concentration of the free base present at any moment. We will call the total original concentration of the imidoester used, both as hydrochloride and as free base, 1 gram molecule in V liters, and the known original concentration of the salt (hydrochloride) of the imidoester used, s gram molecules in V liters. The concentration of the free acid formed by hydrolysis of the salt at any moment t shall be called y gram molecules in V liters, and the amount of imidoester saponified in t minutes, x gram molecules in V liters. Then, at any moment, we have[1]

$$C_{acid} = \frac{y}{V}, \quad C_{salt} = \frac{s - x - y}{V}, \quad C_{base} = \frac{1 - s + y}{V}.$$

Inserting these values in equation (6′), we obtain

$$\frac{s - x - y}{V} = k_{hydrolysis} \times \frac{1 - s + y}{V} \times \frac{y}{V} \qquad (6').$$

For a given experiment, V is a constant. Putting in $K_v = \frac{V}{k_{hydrolysis}}$ and solving for y, we have

$$y = -\frac{1 - s + K_v}{2} + \sqrt{\left(\frac{1 - s + K_v}{2}\right)^2 + K_v(s - x)} \quad (8).$$

Substituting this value in the expression for C_{base} we have

$$C_{base} = \frac{1}{V}\left[\frac{1 - s - K_v}{2} + \sqrt{\left(\frac{1 - s + K_v}{2}\right)^2 + K_v(s - x)}\right] \quad (9).$$

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[1] The imidoesters are such weak bases, compared with ammonia, that the amount of ammonium chloride decomposed by the little free ester present was considered a negligible quantity. The affinity constants are

$$k_{NH_3} = 2 \times 10^{-5}, \quad \text{and} \quad k_{im.est} = 5 \times 10^{-9}$$

and less.

Then equation (II.) becomes

$$\frac{d\frac{x}{v}}{dt} = k_{base} \times \frac{1}{V}\left[\frac{1-s-K_v}{2} + \sqrt{\left(\frac{1-s+K_v}{2}\right)^2 + K_v(s-x)}\right] \quad (10),$$

$$t = \frac{2}{k_{base}}\int\frac{dx}{1-s-K_v+\sqrt{(1-s+K_v)^2+4K_v(s-x)}} \quad (11).$$

Integrating this expression, we obtain

$$k_{base} = \frac{1}{K_v(t_2-t_1)}\left[\sqrt{R-4K_vx_1} - \sqrt{R-4K_vx_2} + (1-s-K_v)\ \text{log nat}\ \frac{\sqrt{R-4K_vx_2}+(1-s-K_v)}{\sqrt{R-4K_vx_1}+(1-s-K_v)}\right] \quad (12),$$

in which $R = (1-s+K_v)^2 + 4K_vs$.

When the hydrochloride of an imidoester is used alone, without an excess of free base, then the free base formed by hydrolysis of the salt has the same concentration as the free acid; for this special, but in practice more common, case, $s = 1$, and the above expression becomes

$$k_{base} = \frac{1}{t_2-t_1}\left[\sqrt{1+\frac{4(1-x_1)}{K_v}} - \sqrt{1+\frac{4(1-x_2)}{K_v}} + \text{log nat}\ \frac{\sqrt{K_v^2+4K\ (1-x_1)}-K_v}{\sqrt{K_v^2+4K_v(1-x_2)}-K_v}\right] \quad (12').$$

Owing to the very small value of K_v, we may simplify this and use

$$k_{base} = \frac{2}{(t_2-t_1)\sqrt{K_v}}\left[\sqrt{1-x_1} - \sqrt{1-x_2}\right] \quad (12'').$$

(3) Equation (III.), $\frac{dx}{dt} = k_{salt} \times C_{salt}$, represents the velocity of the decomposition of imidoesters into ammonia and esters under the influence of acids as directly proportionate to the concentration of the salt present or, for our work in dilute solu-

tions, to that of the positive ions of the imidoesters present at any moment. If we use the same symbols as in (2) to represent the concentrations we find

$$C_{salt} = \frac{s-x-y}{V},$$
$$= \frac{1}{V}\left[s-x+\frac{1-s+K_v}{2}-\sqrt{\left(\frac{1-s+K_v}{2}\right)^2+K_v(s-x)}\right] \quad (13).$$

Substituting this value in (III.), we obtain

$$\frac{d\frac{x}{v}}{dt} = k_{salt} \times \frac{1}{V}\left[s-x+\frac{1-s+K_v}{2}-\sqrt{\left(\frac{1-s+K_v}{2}\right)^2+K_v(s-x)}\right] \quad (14),$$

and

$$t = \frac{1}{k_{salt}}\int\frac{dx}{s-x+\frac{1-s+K^v}{2}-\sqrt{\left(\frac{K_v}{2}\right)^2+(s-x)K_v}} \quad (15).$$

Integrating, we find

$$k_{salt} = \frac{1}{t_2-t_1}\left[\frac{1-s+K_v}{1-s}\log\text{nat}\frac{\sqrt{R-4K_vx_1}-(1-s+K_v)}{\sqrt{R-4K_vx_2}-(1-s+K_v)}+\right.$$
$$\left.\frac{1-s-K_v}{1-s}\log\text{nat}\frac{\sqrt{R-4K_vx_1}+(1-s-K_v}{\sqrt{R-4K_vx_2}+(1-s-K_v}\right] \quad (16),$$

in which expression $R=(1-s+K_v)^2+4K_vs$.

In the calculations, K_v having a very small value, the factors before the logarithms can be dropped.

For the case in which we use the hydrochloride of an imidoester without an excess of the free base, and $s=1$, the above expression becomes indefinite. But for this case, we have

$$C_{salt} = \frac{1}{V}\left[1-x+\frac{K_v}{2}-\sqrt{\left(\frac{K_v}{2}\right)^2+(1-x)K_v}\right] \quad (17).$$

Integrating the corresponding differential equation, we find

$$k_{sa} = \frac{1}{t_2 - t_1}\left[\log \text{nat} \frac{2-2x_1+K_v - \sqrt{K^2_v+4K_v(1-x_1)}}{2-2x_2+K_v - \sqrt{K^2_v+4K_v(1-x_2)}} - \frac{1}{\sqrt{\frac{1-x_1}{K_v}+0.25}-0.5} + \frac{1}{\sqrt{\frac{1-x_2}{K_v}+0.25}-0.5}\right] \quad (18).$$

Discarding the functions which do not affect the arithmetical results, we have, more simply,

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\log \text{nat} \frac{1-x_1-\sqrt{(1-x_1)K_v}}{1-x_2-\sqrt{(1-x_2)K_v}} - \sqrt{\frac{K_v}{1-x_1}} + \sqrt{\frac{K_v}{1-x_2}}\right] \quad (18').$$

For less rigorous calculations, when the salts are used *without an excess of free base*, the degree of hydrolysis being very small, we can consider practically the whole substance to be salt, and use, more simply,

$$k_v = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C-x_1}{C-x_2}.$$

(4) If we wish to take into consideration the simultaneous saponification of the imidoester salt into ammonia and an acid ester and the decomposition of the free base, at a very much slower rate (see Part VII.), into alcohol and a nitrile, we would have

$$\frac{dx}{dt} = k_{salt}\, C_{salt} + k_{base}\, C_{base} \quad \text{(III')},$$

where k_{salt} is the velocity constant for the saponification of the salt or positive ion of the imidoester, and k_{base} is the constant determined in Part VII. for the decomposition of the non-ionized free base into a nitrile and an alcohol, provided the decomposition of the base remains unaffected by the presence of the salt. The results obtained indicate that such is the case. If we use the same symbols as in (2) and (3), C_{salt} has the value given in equation (13); C_{base}, that given in equation (9).

Then

$$\frac{d\frac{x}{v}}{dt} = k_{salt}\,\frac{1}{V}\left[s - x + \frac{1-s+K_v}{2} - \sqrt{\left(\frac{1-s+K_v}{2}\right)^2 + K_v(s-x)}\right] + k_{base}\,\frac{1}{V}\left[\frac{1-s-K_v}{2} + \sqrt{\left(\frac{1-s+K_v}{2}\right)^2 + K_v(s-x)}\right] \quad (19),$$

$$t = \int \frac{dx}{k_{salt}\left[s-x+\frac{1-s+K_v}{2} - \sqrt{\left(\frac{1-s+K_v}{2}\right)^2 + K_v(s-x}\right]} + \frac{dx}{k_{base}\left[\frac{1-s-K_v}{2} + \sqrt{\left(\frac{1-s+K_v}{2}\right)^2 + K_v(s-x)}\right]} \quad (20).$$

Integrating, we obtain

$$t_2 - t_1 = \frac{1-s-K_v}{k_{salt} - sk_{salt} - K_vk_{base}} \times \log\text{ nat}\,\frac{\sqrt{R-4K_vx_1} + (1-s-K^v)}{\sqrt{R-4K_vx_2} + (1-s-K_v)} + \frac{k_{salt}\,(1-s+K_v) - 2K_vk_{base}}{k_{salt}\,(k_{salt} - sk_{salt} - K_vk_{base})} \times \log\text{ nat}\,\frac{\sqrt{R-4K_vx_1} - (1-s+K_v) + \frac{2K_vk_{base}}{k_{salt}}}{\sqrt{R-4K_vx_2} - (1-s+K_v) + \frac{2K_vk_{base}}{k_{salt}}} \quad (21),$$

in which $R = (1-s+K_v)^2 + 4K_vs$.

Some of the functions can be dropped in the application, as not affecting the numerical result; we have, more simply,

$$t_2 - t_1 = \frac{1}{k_{salt}} \times \log\text{ nat}\,\frac{\sqrt{R-4K_vx_1} - (1-s+K_v) + \frac{2K_vk_{base}}{k_{salt}}}{\sqrt{R-4K_vx_2}\,(1 - - s + K_v) + \frac{2K_vk_{base}}{k_{salt}}} \quad (21').$$

The expression $\frac{2K_v k_{base}}{k_{salt}}$ in the logarithmic term must be calculated by using the constant k_{salt} as previously determined in the absence of an excess of the free base, and the constant k_{base} as determined in Part VII. for the base in the absence of the salt.

In the following tables sufficient of the experimental results will be summarized to enable us to distinguish between the above possibilities, and to recognize sharply the actual reacting substance in the formation of ammonia and an alkyl benzoate when an imidoester is decomposed by water in the presence of dilute acid.

In the first table are given constants calculated according to the equations (12′) and (12) to see if the velocity of the reaction is proportionate to the concentration of the free base always present. Each series of numbers in a line following k_{base} represents the results at different time intervals of one experiment. Under the groups marked (*a*) are given experiments with the hydrochlorides of the imidoesters present alone, the free base present being formed wholly by the hydrolytic dissociation of the salts by water; under (*b*) are given the results of experiments with the hydrochlorides in the presence of an added excess of the free bases.

Table I.

(1) *Methyl Imidobenzoate*, $C_6H_5C(:NH)OCH_3$.
  (*a*) 0.05 molar salt, at 25°,[1] total time, 400 minutes.
    $10^3\ k_{base}$: 771; 676; 560; 460.
  (*b*) 0.05 molar salt, 0.0125 molar free base, 25°, 180 minutes.
    $10^3\ k_{base}$: 19.5; 16.5; 15.1; 12.9.
    0.05 molar salt, 0.01 molar free base, 25°, 445 minutes.
    $10^3\ k_{base}$: 20.1; 16.0————10.15.
(2) *Ethyl Imidobenzoate*, $C_6H_5C(NH)OC_2H_5$.
  (*a*) 0.05 molar salt, 25°, 720 minutes.
    $10^3\ k_{base}$: 620; 597; 560; 513; 437.
  (*b*) 0.0375 molar salt, 0.0125 molar base, 25°, 250 minutes.
    $10^3\ k_{base}$: 458; 429; 400; 413; 385.

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[1] The temperature was always kept constant within ± 0.01°, unless otherwise stated.

Table I—(Continued).

(3) *Methyl Imido-m-nitrobenzoate*, $NO_2C_6H_4C(NH)OCH_3$.

(*a*) 0.05 molar salt, 18°, 108 minutes.

$10^3\ k_{base}$: 1170; 1014; 782; 692.

(*b*) 0.05 molar salt, 0.005 molar base, 18°, 107 minutes.

$10^3\ k_{base}$: 194; 146; 104.

It is obvious that k_{base} is not a constant in any series and not constant for the same reaction under varying original concentrations of the free base. Evidently the reaction is not a function of the concentration of the free imidoester.[1]

In Table II. are given some of the constants, k_{subst}, calculated according to equation (7) to see if the velocity of the reaction is proportionate to the total substance present, salt and base indifferently. When salts are used alone (Series *a*), the degree of hydrolysis being very small (usually only a very few per cent of the substance), there is not sufficient difference between the concentrations of the salt and the total substance to appear in the calculations to any extent; if the one gives a real constant, the other will also. But a sharp distinction can be made by comparing these constants (Series *a*) with those obtained in Series (*b*) where the salt and an excess of the free base are used; in these cases there is, of course, a decided difference in the concentration of the salt and the total substance.

Table II.

(1) *Methyl Imidobenzoate*, $C_6H_5C(NH)OCH_3$.

(*a*) 0.025 molar hydrochloride, 25°, 390 minutes.

$10^5\ k_{subst}$: (520); (610); 587; 582; 580; 576; 578; 576. Mean: 580.

0.05 molar hydrochloride, 25°, 440 minutes.

$10^5\ k_{subst}$: 557; 569; 539; 523; 514; 534. Mean: 539.

0.05 molar hydrochloride, 25°, 400 minutes.

$10^5\ k_{subst}$: (589); 548; 543; 536; 543; 541. Mean: 542.

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[1] **Reactions in which the free bases in hydrolyzed salt solutions were found to be the only reacting ingredient were described in This Journal, 31, 458 (1904) by Stieglitz and Upson.**

Table II—(Continued).

(*b*) 0.05 molar hydrochloride, 0.0125 molar base, 25°, 180 minutes.

$10^5\ k_{subst}$: 465; 424; 421; 396.

0.04 molar salt, 0.01 molar base, 25°, 420 minutes.

$10^5\ k_{subst}$: 532; 463; 438; 403; 387; 375; 364; 318.

(2) *Ethyl Imidobenzoate*, $C_6H_5C(NH)OC_2H_5$.

(*a*) 0.05 molar hydrochloride, 25°, 620 minutes.

$10^5\ k_{subst}$: 313; 310; 314; 320. Mean: 314.

0.05 molar salt, 25°, 300 minutes.

$10^5\ k_{subst}$: 309; 318; 309. Mean: 312.

0.05 molar salt, 25°, 540 minutes.

$10^5\ k_{subst}$: 304; 302; 306; 304; 306. Mean: 304.

0.05 molar salt, 25°, 570 minutes.

$10^5\ k_{subst}$: (266); 302; 302; 304; 304. Mean: 303.

(*b*) 0.0375 molar salt, 0.0125 molar base, 25°, 250 minutes.

$10^5\ k_{subst}$: 226; 221; 216.

(3) *Methyl Imido-m-nitrobenzoate*, $m\text{-}NO_2C_6H_4C(NH)OCH_3$.

(*a*) 0.05 molar salt, 18°, 108 minutes.

$10^4\ k_{subst}$: 251; 251; 250; 241; 245; 238; 239; 237. Mean: 244.

0.025 molar salt, 18°, 109 minutes.

$10^4\ k_{subst}$: 251; 246; 239; 249; 243; 240; 234; 234. Mean: 242.

(*b*) 0.05 molar salt, 0.005 molar base,[1] 18°, 67 minutes.

$10^4\ k_{subst}$: 235; 225; 221; 214; 207; 201.

The contrast in the values of the series (*a*) and (*b*) for each ester, and a survey of the results obtained in a single long experiment of Series (*b*) (*e. g.*, experiment 1*b*), show positively that the velocity of the reaction under discussion is not proportionate to the concentration of the total substance present.

In the third table are given the constants calculated according to equations (16), (18′), and (21′), to see if the velocity of the reaction is proportionate simply to the concentration of the salt present. The series under (*a*) represent again velocities where pure salts were used, under (*b*) are given the constants for experiments in which an excess of free base is present, k_{salt}

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[1] This free base is very difficultly soluble.

representing the constant calculated according to equation (16) without any correction for the simultaneous, exceedingly slow decomposition of the free base into a nitrile and an alcohol, and k'_{salt} representing the constant calculated according to equation (21′) where it is assumed that the free base is decomposing very slowly of itself, exactly as it does in the absence of the salt, according to the constant for this reaction determined in Part VII.

Table III.

(1) *Methyl Imidobenzoate*, $C_6H_5C(NH)OCH_3$.

(*a*) 0.025 molar salt, 25°, 390 minutes.

10^5 k_{salt}: (527); (669); 610; 600; 595; 590; 592; 590. Mean: 596.

0.05 molar salt, 25°, 440 minutes.

10^5 k_{salt}: 560; 573; 543; 530; 520; 541; 538. Mean: 544.

0.05 molar salt, 25°, 400 minutes.

10^5 k_{salt}: 592; 550; 548; 541; 550; 550. Mean: 555.

(*b*) 0.05 molar salt, 0.0125 molar base, 25°, 180 minutes.

10^5 k_{salt}: 603; 552; 608; 584. Mean: 587.

10^5 k'_{salt}: 593; 543; 596; 571. Mean: 576.

0.04 molar salt, 0.01 molar base, 25°, 429 minutes.

10^5 k_{salt}: 553; 566; 585; 598; 616; 579; 605. Mean: 586.

10^5 k'_{salt}: 545; 558; 571; 580; 591; 560; 570. Mean: 566.

Mean, Series (*a*): $k_{salt} = 565$.

Mean, Series (*b*): $k_{salt} = 586$, $k'_{salt} = 571$.

(2) *Ethyl Imidobenzoate*: $C_6H_5C(NH)OC_2H_5$.

(*a*) 0.05 molar salt, 25°, 620 minutes.

10^5 k_{salt}: 313; 312; 316; 323. Mean: 316.

0.05 molar salt, 25°, 300 minutes.

10^5 k_{salt}: 310; 320; 310. Mean: 313.

0.05 molar salt, 25°, 540 minutes.

10^5 k_{salt}: 306; 304; 307; 306; 307. Mean: 306.

0.05 molar salt, 25°, 570 minutes.

10^5 k_{salt}: 310; 304; 304; 306; 306. Mean: 306.

(*b*) 0.0375 molar salt, 0.0125 molar base, 25°, 250 minutes.

10^5 k_{salt}: 287; 299; 305. Mean: 297.

Mean, Series (*a*): $k_{salt} = 310$. Series (*b*): $k_{salt} = 297$.

Table III—(Continued).

(3) *Methyl Imido-m-nitrobenzoate.* $m\text{-}NO_2C_6H_4C(NH)OCH_3$.

(*a*) 0.05 molar salt, 18°, 108 minutes.

$10^4\ k_{salt}$: 259; 258; 261; 256; 253; 251; 253; 252. Mean: 255.

0.025 molar salt, 18°, 109 minutes.

$10^4\ k_{salt}$: 264; 259; 253; 265; 259; 258; 253; 256. Mean: 258.

(*b*) 0.05 molar salt, 0.005 molar base, 18°, 67 minutes.

$10^4\ k_{salt}$: 265; 258; 259; 257; 256; 258. Mean: 259.

$10^4\ k_{salt}$: 268; 260; 261; 258; 257; 2623. Mean: 261.

Mean, Series (*a*): $k_{salt} = 257$. Series (*b*): $k_{salt} = 259$, $k'_{salt} = 261$.

The agreement in the results for the constants obtained in each experiment shows that they represent real constants. The comparison of the constants obtained for a given ester in the presence or the absence of an excess of free base shows also that the reaction velocity in all cases is strictly proportionate to the concentration of the salt (the positive ions) present at any moment; thus, for methyl imidobenzoate (Series 1), the mean velocity constant in the absence of an excess of the free base is $k_{salt} = 0.00565$; in the presence of the free base, $k_{salt} = 0.00585$ or $k'_{salt} = 0.00571$, respectively, according to whether or not a correction is made for the simultaneous, very slow decomposition of the free base in a different direction. For ethyl imidobenzoate the average constants are $k_{salt} = 0.00310$ and $k_{salt} = 0.00297$; for methyl imido-*m*-nitrobenzoate the averages are $k_{salt} = 0.0257$ and $k_{salt} = 0.0259$ and $k'_{salt} = 0.0261$.

From Tables I., II., III., which represent only a part of many similar experiments leading to the same conclusion, it appears certain, therefore, that the addition of hydrochloric acid, which so greatly accelerates the velocity of saponification of an imidoester into ammonia and an ester does so simply through salt formation, that is, the salt decomposes very much faster in this direction than the free base does. In the dilute solutions used, practically all of the salt is ionized and so it is obvious that it is the positive ion which is the active constituent, reacting with water with a constant velocity at a given temperature.[1] In the aqueous solution of the free base, we have a very few of these positive ions, so few, however, that their decomposition is barely discernible as compared with the decomposition of the nonionized base, which is present in largest quantity and which gives, according to equation (1), a nitrile and an alcohol. The addition of an acid, with the formation of easily ionizable salts, greatly increases the concentration of the positive ions, and their reaction with water, expressed in equation (2), leading to the formation of an ester and ammonium ions, becomes the predominating one. We must therefore write the reaction as

$$CH_5C(\overset{+}{N}H_2)OCH_3 + H_2O \rightarrow C_6H_5COOCH_3 + \overset{+}{N}H_4 \quad (2')$$

The accelerating, or let us call it the catalytic, action of the hydrochloric acid has, then, been proved to be due in this case simply to the formation of positive ions, that is, to the formation of different molecules of different energy content and of greater reactivity or instability. Now, if this should prove to be the correct explanation of the catalytic actions of acids in general, it is obvious that by this same power of forming salts and positive ions they should be liable, also, in certain cases to *retard* action instead of accelerating it, provided the positive ion or salt is less *reactive or more stable* than the free base. That must be a consequence of this theory and we already have brought out its complete experimental confirmation and elaboration in the work carried out with Dr. Upson on the rearrangement of the aminophenylalkyl carbonates,[2] an investigation which was undertaken expressly in order to test rigorously the correctness of this conclusion.[3] As that investigation forms a part of the present argument, it is desired to incorporate in a very brief summary the most important results of the work. The aminophenylalkyl carbonates rearrange spontaneously into oxyphenylurethanes, according to

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[1] Dr. Schlesinger's work on the velocities of the reactions and the degrees of ionization of the salts used, completed (1905) since the writing of this (1904), fully confirms the conclusion that only the ions of the salt are decomposed by water, as will be described in one of the next papers.

[2] This Journal, **31**, 458 (1904).

[3] *Ibid.*, 461.

$$\mathrm{NH_2C_6H_4OCO_2C_2H_5} \leftarrow \mathrm{C_2H_5O_2CNHC_6H_4OH} \qquad (22),$$

by a shifting of the carbethoxyl group from the oxygen to the nitrogen atom.

The hydrochlorides of these amines are hydrolyzed in aqueous solution according to

$$\mathrm{ClH_3NC_6H_4OCO_2C_2H_5 + H_2O} \rightleftarrows \mathrm{HOH_3NC_6H_4OCO_2C_2H_5 + HCl} \qquad (23).$$

Hydrochloric acid retards, but does not prevent, the rearrangement expressed in (22), and it was suspected that it retards it quantitatively by salt formation only; that in the aqueous solution of the salts the rearrangement would still proceed in rigorous proportion to the concentration of the small amount of free base present according to (23) and would ultimately complete itself. The experimental results proved that such is actually the case, the action being followed with six bases through ten hours and the velocity remaining constantly proportionate to the small concentration of the free base in the presence of the continually accumulating acid.

Briefly, then, hydrochloric acid has been shown to accelerate or retard action quantitatively *through salt or ion formation. Now these enormous changes in speeds of reaction are really the main characteristic of catalytic action*; it remains, however, to determine whether the two other characteristics important for *certain* cases, are also in agreement with this conception, rigorously applied; first, that the catalyzer need not appear to enter into combination with any of the substances present and, second, that in a reversible reaction it need not measurably change the final condition of equilibrium. We shall now test this view by the rigorous application of the above principle of salt or, rather, ion formation to the well-known catalysis of methyl acetate, to which the last two characteristics mentioned are known to apply.

III. The Catalysis of Methyl Acetate.

The intimate connection of this case with the work on the imidoesters is readily recognized as follows: we found above that for imidoesters,

$$\frac{dx}{dt} = k \times C_{pos.\ ion.} \qquad \text{(III.).}^1$$

But

$$C_{pos.\ ion.} = K_{hydrolysis} \times C_{base} \times C_H \qquad (6),^2$$

and therefore

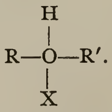
$$\frac{dx}{dt} = k \times K_{hydrolysis} \times C_{base} \times C_H \qquad (24),$$

$$= k' \times C_{base} \times C_H \qquad (24').$$

But this is the well-known velocity equation for the catalysis of esters in the presence of an acid, C_{ester} being substituted for C_{base},

$$\frac{dx}{dt} = k \times C_{ester} \times C_H \qquad (25),$$

and so, if the ester could form salts with an acid, its saponification could undoubtedly be due to the decomposition of its positive ions by water. This important link in the argument has been supplied, since the work was first undertaken, by the discoveries by Baeyer[3] and others that esters do combine with acids to give compounds, which, though very unstable, are unmistakable salts. They are almost certainly oxonium salts, possibly, but less likely,[4] carbonium salts; either conception will do for the application of our conclusions, and we shall use the much more likely view that they are oxonium salts,



$$\mathrm{R{-}\overset{\displaystyle H}{\underset{\displaystyle X}{O}}{-}R'}.$$

It may be added that Coehn[5] has proved that these compounds are true salts, capable of ionization, by showing that in a solution of dimethylpyrone in hydrochloric acid the pyrone migrates, under the influence of an electric current, to the negative pole as a positive ion of an oxonium base. It may also

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[1] Pages 34 and 46.

[2] Page 35.

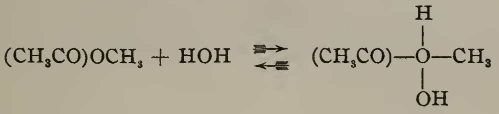
[3] Ber. d. chem. Ges., **34**, 2679 (1901), etc.

[4] Stieglitz and Edith Barnard: J. Am. Chem. Soc., **27**, 1016 (1905).

[5] Ber. d. chem. Ges., **35**, 2673 (1902).

be recalled that methyl acetate gives with hydrogen chloride, in the absence of water, methyl chloride, exactly as the hydrochlorides of the imidoesters do when they are heated to 100°–130° in the absence of water.

Methyl acetate must then form with water an oxonium base in the same way that ammonia combines with water to form ammonium hydroxide,

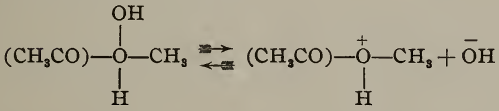


$$(CH_3CO)OCH_3 + HOH \rightleftarrows (CH_3CO)\text{—}\overset{\overset{\Large H}{|}}{\underset{\underset{\Large OH}{|}}{O}}\text{—}CH_3 \quad (26),$$

and

$$C_{ester} \times C_H \times C_{OH} = k' \times C_{base} \qquad (27).$$

The base ionizes according to



$$(CH_3CO)\text{—}\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large H}{|}}{O}}\text{—}CH_3 \rightleftarrows (CH_3CO)\text{—}\overset{+}{\underset{\underset{\Large H}{|}}{O}}\text{—}CH_3 + \overset{-}{O}H \quad (28),$$

for which we have

$$C_{est.\,pos.\,ion} \times C_{OH} = k_{base} \times C_{base} \qquad (29).$$

Combining (27) and (29), we have

$$C_{est.\,pos.\,ion} = \frac{k_{base}}{k'} \times C_{ester} \times C_H \qquad (30).[1]$$

Now, if, as was proved for the imidoesters, it is only the positive ions which react with water to give acetic acid and methyl alcohol, according to the fundamental equation

$$CH_3COOCH_3 + HOH \rightarrow CH_3COOH + CH_3OH \quad (31),$$

we would have for the velocity of this reaction of saponification

$$\frac{dx}{dt} = k_s \times C_{est.\,pos.\,ion} \times C_H \times C_{OH} \qquad (32).[2]$$

For water,

$$C_H \times C_{OH} = k_w \times C_{H_2O} \qquad (33).$$

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[1] See footnote, page 50.

[2] $C_{est.\,pos.\,ion}$ is a function of x.

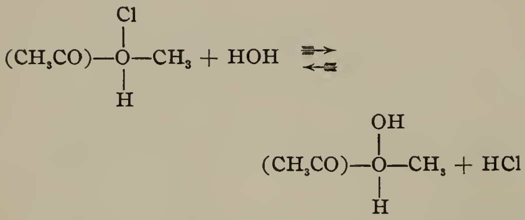
Substituting the values of (30) and (33) in (32), we have

$$\frac{dx}{dt} = k_s \times \frac{k_{base}}{k'} \times C_{ester} \times C_H \times k_w \times C_{H_2O} \qquad (34),$$

$$= K_s \times C_{ester} \times C_{H_2O} \times C_H \qquad (34'),$$

as representing the velocity of the decomposition of methyl acetate by water in the absence of any acid.

If we add hydrochloric acid to the mixture of methyl acetate and water, we obtain the hydrochloride of the oxonium base, but the salt is almost completely hydrolyzed according to the equation



$$(CH_3CO)\text{—}\overset{\displaystyle Cl}{\underset{\displaystyle H}{O}}\text{—}CH_3 + HOH \rightleftarrows (CH_3CO)\text{—}\overset{\displaystyle OH}{\underset{\displaystyle H}{O}}\text{—}CH_3 + HCl$$

(35).

In such a solution we would have for the free base present,[1] according to (27), (29), and (30),

$$C'_{est.\,pos.\,ion} = \frac{k_{base}}{k'} \times C_{ester} \times C'_H \qquad (36).$$

Substituting the new value for $C_{est.\,pos.\,ion}$ in the velocity equation (32), we have, with the aid of (33), for the velocity of decomposition of methyl acetate in the presence of hydrochloric acid,

$$\frac{dx}{dt} = k_s \times \frac{k_{base}}{k'} \times C_{ester} \times C'_H \times k_w \times C_{H_2O} \qquad (37),$$

$$= K_s \times C_{ester} \times C'_H \times C_{H_2O} \qquad (37').$$

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[1] As the amount of salt formed is exceedingly small, hydrolysis being practically complete for such exceedingly weak bases, the concentration of the nonionized ester, C_{ester}, would not be measurably changed. It should be recalled that Walden (Ber. d. chem. Ges., **34**, 4185 (1901)) and Walker (*Ibid.*, **34**, 4115 (1901)) found that the oxonium bases are extremely weak. For instance, the affinity constant for dimethylpyrone is about 3×10^{-14}. Dimethylpyrone being one of the most pronounced bases among the oxonium bases. the affinity constant for esters undoubtedly must be much smaller.

By comparison with the velocity equation (34′) for the decomposition of the acetate in the presence of water alone, equation (37′) shows us that the velocity is affected by the addition of the acid only by the increased concentration of the hydrogen ions (from C_H to C'_H) and proportionately to this change, which is in accord with the experimental facts.

We must now consider the well-known fact that the decomposition of methyl acetate by water is a reversible reaction, acetic acid and methyl alcohol giving methyl acetate and water, according to

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \qquad (38)$$

and the fact that the velocity of this reaction is also accelerated by the addition of hydrochloric acid. Following out our conception rigorously, that hydrochloric acid acts only through salt, and subsequent ion, formation, we must conclude that this increased velocity must be due to weak basic properties of the acetic acid or the methyl alcohol and to consequent salt formation and ionization through the agency of the hydrochloric acid. Although methyl alcohol undoubtedly also has the power to form oxonium salts with acids,[1] the formation of methyl acetate must be due primarily to the minimal basic properties of acetic acid.[2]

It is no novel conception to find a compound exhibiting the amphoteric character of base and acid[3] and especially in the

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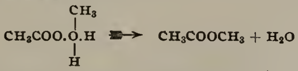
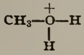
[1] Baeyer: *Loc. cit.*

[2] If it were due to the basic properties of methyl alcohol and the primary formation of an acetate of methyl alcohol, the velocity of the formation of the ester would depend on the presence of the *nonionized* acetate,

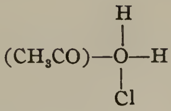


$$CH_3COO.\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{O}}.H \rightleftharpoons CH_3COOCH_3 + H_2O \qquad (39).$$

It is not conceivable that the *separate* ions of this salt,  $CH_3{-}\overset{+}{\underset{\underset{H}{|}}{O}}{-}H$ and $CH_3C\overline{OO}$, could break down into methyl acetate, since each ion contains either no methyl or no acetate group and jointly they would give again the nonionized salt of equation (39). But there must be more nonionized acetate formed in the absence of a stronger acid, like hydrochloric acid, than in its presence; hence, the latter would have to retard, rather than accelerate, the esterification, if this depended on the basic functions of methyl alcohol.

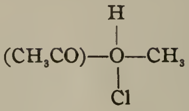
[3] There are excellent reasons, in fact, for considering that all hydroxides known, even our strongest acids, like HNO_3, H_2SO_4, $HMnO_4$, are amphoteric and that some of their most important properties, for instance, their oxidizing power, are due to their *basic* ionization. See Stieglitz: "Qualitative Analysis," University of Chicago, 1905, p. 55.

case of so weak an acid as acetic acid. It is clear, too, that the salts



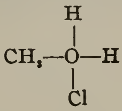
$(CH_3CO)-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{O}}-H$

and



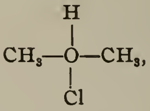
$(CH_3CO)-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{O}}-CH_3$

are entirely analogous to



$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{O}}-H$

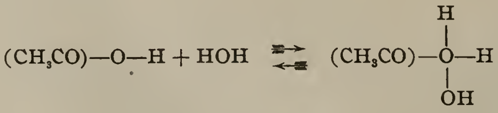
and



$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{O}}-CH_3,$

the oxonium salts of methyl alcohol and methyl ether, the latter being the first oxonium salt known.[1] In experimental support of the basic functions of acetic acid, Rosenheim[2] found that acetic and other organic acids must form oxonium salts, for there is a perfect parallelism in their behavior and that of their esters towards chlorides, like antimony pentachloride. Euler[3] also arrived at the conclusion that the esterification of acetic acid must be due primarily to basic properties of acetic acid.

Applying rigorously then to esterification our fundamental conception that the accelerating action of hydrochloric acid must be due to the formation of a salt with a basic oxide, and finding that in the present case it must be the acetic acid that acts as a base, we have for acetic acid, forming an oxonium base with water,



$$(CH_3CO)-O-H + HOH \rightleftarrows (CH_3CO)-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{O}}-H \quad (40),$$

and

$$C_{ac.\ acid} \times C_H \times C_{OH} = k'_1 \times C_{ac.\ base} \qquad (41);$$

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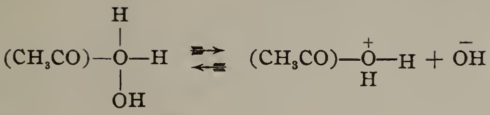
[1] Friedel: Bull. Soc. Chim., **24**, 160 (1875).

[2] Ber. d. chem. Ges., **34**, 3377 (1901); **35**, 1115 (1902).

[3] Z. physik. Chem., **36**, 641 (1901).

and also



$$(CH_3CO)-\overset{\displaystyle H}{\underset{\displaystyle OH}{O}}-H \rightleftarrows (CH_3CO)-\underset{H}{\overset{+}{O}}-H + \overset{-}{O}H \quad (42),$$

giving

$$C_{ac.\ pos.\ ion} \times C_{OH} = k'_{base} \times C_{ac.\ base} \quad (43).$$

Dividing equation (43) by (41), we have

$$C_{ac.\ pos.\ ion} = \frac{k'_{base}}{k'_1} \times C_{ac.\ acid} \times C_H \quad (44).$$

If, in the esterification of acetic acid by methyl alcohol, as found for the imidoesters,[1] it is only the positive acet ion which reacts with the methyl alcohol, then we have for the velocity of esterification, according to equation (38),

$$\frac{dx}{dt} = k_e \times C_{ac.\ pos.\ ion} \times C_H \times C_{OCH_3} \quad (45).$$

For methyl alcohol we have

$$CH_3OH \rightleftarrows \overset{-}{CH_3O} + \overset{+}{H} \quad (46),$$

and

$$C_H \times C_{OCH_3} = k_{alc} \times C_{CH_3OH} \quad (47).$$

Introducing the values found in equations (44) and (47) into the velocity equation (45), we obtain for the speed of esterification in the absence of hydrochloric acid

$$\frac{dx}{dt} = k_e \times \frac{k_{base}}{k'_1} \times C_{ac. acid} \times C_H \times k_{alc} \times C_{CH_3OH} \quad (48),$$

$$= K_e \times C_{ac.\ acid} \times C_H \times C_{CH_3OH} \quad (48').$$

On adding hydrochloric acid to the system of acetic acid and methyl alcohol as given in equation (38), we would obtain a little of the hydrochloride of the oxonium base of acetic acid, the salt being largely hydrolyzed according to

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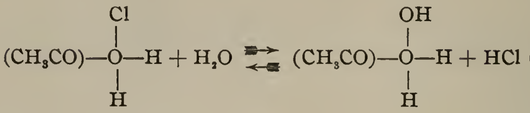
[1] That the positive ions of the imidoesters form the "active mass" in other interactions than that with water is proved, as was anticipated, by the observations of Miss K. Blunt that, in the formation of *amidines* from imidoesters by the action of ammonia, the amidine formation is due to the action of ammonia on the positive imidoester ions, even though these are present only in *minimal*, but rigorously *calculable*, quantities. The results will be published in a later paper.



$$(CH_3CO)-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle Cl}{|}}{O}}-H + H_2O \rightleftarrows (CH_3CO)-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{O}}-H + HCl \quad (49).$$

According to equations (41) and (43), we must have for the free base in the hydrolyzed solution[1]

$$C_{ac.\,acid} \times C'_H \times C'_{OH} = k'_1 \times C'_{ac.\,base} \qquad (41'),$$

and

$$C'_{ac.\,pos.\,ion} \times C'_{OH} = k'_{base} \times C'_{ac.\,base} \qquad (43').$$

Dividing (43′) by (41′), we have

$$C'_{ac.\,pos.\,ion} = \frac{k'_{base}}{k_1} C_{ac.\,acid} \times C'_H \qquad (44').$$

Introducing the new concentration of the reacting positive ions of acetic acid into the velocity equation (45), we obtain, for the new condition,

$$\frac{dx}{dt} = k_e \times C'_{ac.\,pos.\,ions} \times C'_H \times C'_{OCH_3} \qquad (50),$$

$$= k_e \times \frac{k'_{base}}{k'_1} \times C_{ac.\,acid} \times C'_H \times k_{alc} \times C_{CH_3OH} \qquad (51),$$

$$= K_e \times C_{ac.\,acid} \times C'_H \times C_{CH_3OH} \qquad (51'),$$

as representing the velocity of esterification in the presence of hydrochloric acid.

By comparing equations (48′) and (51′), representing the velocities of esterification in the absence and the presence of hydrochloric acid, we learn from equation (51′) that the velocity is affected by the addition of the acid only by the increased concentration of the hydrogen ions (from C_H to C_H) and proportionately to this change. This conclusion, based on the theoretical development of the esterification catalysis as one of salt and ion formation, is in agreement with the well-known experimental facts.

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[1] $C_{ac.\,acid}$ is not *measurably* changed, as explained in footnote, p. 50. The same is true for C_{CH_3OH} in equation (47).

The condition for equilibrium in the reversible process of saponification and esterification,

$$CH_3COOCH_3 + H_2O \rightleftarrows CH_3COOH + CH_3OH \quad (31 \text{ and } 38),$$

is that the velocity of saponification should equal the velocity of esterification, and in the absence of hydrochloric acid we have, according to (34′) and (48′),

$$K_s \times C_{ester} \times C_{HOH} \times C_H = K_e \times C_{ac.\,acid} \times C_H \times C_{CH_3OH} \quad (52).$$

In the presence of hydrochloric acid, the condition of equilibrium follows from equating the expressions in (37′) and (51′):

$$K_s \times C_{ester} \times C_{HOH} \times C'_H = K_e \times C_{ac.\,acid} \times C'_H \times C_{CH_3OH} \quad (53).$$

The addition of hydrochloric acid would therefore, through salt and ion formation, accelerate the reactions in the reversed directions in the same proportions, and therefore it would not affect the final condition of equilibrium measurably; from both equations we get, by canceling the concentration of the hydrogen ions on both sides of each equation, the same expression for the condition of equilibrium,

$$K_s \times C_{ester} \times C_{HOH} = K_e \times C_{ac.\,acid} \times C_{CH_3OH} \quad (54),$$

which agrees with the results of experiment.

It is plain, from the above equations, that we may substitute any acid whatever for hydrochloric acid; its action would be strictly proportionate to the concentration of its hydrogen ions. The equations also bring out clearly the fact that the slow saponifying power of water itself is proportionate to its small concentration of hydrogen ions and that it is a catalyzer just to this extent.

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[1] See Euler (Z. physik. Chem., 36, 641 (1901), who pointed out that a catalyzer does not accelerate a reaction which would go of itself, but that the catalyzer is necessary also to allow the reaction to start and proceed at all.

It is clear, then, that the explanation that an acid accelerates an action simply through salt and ion formation, as was proved experimentally for imidoesters, may be extended to the catalysis of the acid esters, and, without a single new assumption, by the application of the ordinary laws of equilibrium it is found to be in perfect harmony with the three characteristic features of this catalysis: (1) the acceleration is proportionate to the concentration of the hydrogen ions present; (2) the acid does not appear to combine with any of the substances involved in the reaction; and (3) the ultimate condition of equilibrium is not measurably modified in the system. The acid does not *appear* to combine with the ester or the organic acid, simply because the salts are almost completely hydrolyzed under the conditions of the experiment and only very small quantities of the salts and their positive ions exist at any moment, owing to the extremely small affinity constants of the oxonium bases. But still the concentration of the active substance, the positive ion, would always remain proportionate to the concentration of hydrogen ions and the speed of change be proportionately accelerated, no matter how small the order of the actual concentration of the positive ions.

It must be added that unless the concentration of the salt and the positive ions at any moment were exceedingly small the final condition of equilibrium between ester, water, organic acid, and alcohol must be measurably affected by the addition of an acid, since the concentrations of the ester and of the organic acid would be decreased in somewhat different degrees if there were appreciable salt-formation.[1] The second and third characteristics of the catalysis of methyl acetate are therefore indissolubly connected. This would follow, of course, also from the consideration of the energy changes involved in these conditions. *They can be characteristic, consequently, only of such catalytic actions by acids (and bases) in which salts are formed to an extent beyond our methods of measurement, and they are never rigorously true.*

The first characteristic that the acceleration must be proportionate to the concentration of the catalytic agent likewise can only be true for the limiting case of a practically complete hydrolysis, as is seen from the fundamental hydrolysis equation (6) and as is borne out by the behavior of the imidoesters.

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[1] Footnotes, pp. 50 and 54.

The only fundamental property, consequently, which is necessarily common to all catalytic action by chemical reagents such as acids and which is really characteristic of catalysis is an ACCELERATION,[1] in a positive or negative sense, and this acceleration is due and proportionate to salt and ion formation. A perfectly similar conception applies, of course, to the action of alkalis and other chemical catalyzers, and unquestionably will apply to all kinds of catalyzers in the sense that they simply increase the concentration or active mass of a reacting component. The three other characteristics discussed above should then be considered incidental only to special, although important, conditions, in which the main feature, the acceleration, is produced by exactly the same change, salt and ion formation, but in which the imperfections of our methods of measurement still conceal the minimal but important changes in composition and equilibrium produced by the catalyzer.

It may be pointed out, here, that this explanation of catalytic action as due to the formation of salts and ions of greater or less stability or reactivity than the free bases or acids makes these actions, taken from the field of organic chemistry, appear simply as instances of well-known changes found in the realm of inorganic chemistry, where changes of reactivity and stability through salt formation and ionization are numberless; hydrochloric acid, added to ammonia, retards enormously the production and loss of ammonia, accelerates all actions in which ammonium ions are involved; potassium hydroxide retards the loss of carbonic acid from aqueous solutions, facilitates the production of carbonates. These are rough illustrations of the fact that salt formation changes the speed of reactions most decidedly. *Only when the salt formation is not obvious are we accustomed to speak of the change as proceeding "catalytically."*

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[1] Page 30; *vide* also Vol. IV., Report of the Congress of Arts and Science, p. 278.

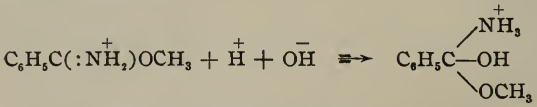
IV. The Mechanism of the Catalysis of Imidoesters and of Esters by Aqueous Acids.

Having established the fact that the accelerating action of hydrochloric acid in the decomposition of the imidoesters by water is directly proportionate to the positive ions formed with the imidoester, and that the conception of salt formation between hydrochloric acid and ordinary esters and organic acids, the last two acting as oxonium bases, is also in complete accord with the fundamental facts and gives us a rational theory for their catalysis, we may well ask how such changes in velocity of reactions must be considered from the point of view of the molecular structure of the compounds under discussion. The imidoesters will be considered first.

The decomposition of methyl imidobenzoate which is accelerated by hydrochloric acid is the following:

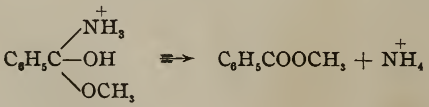
$$C_6H_5C(:\overset{+}{N}H_2)OCH_3 + HOH \rightleftharpoons C_6H_5COOCH_3 + \overset{+}{N}H_4 \quad (2').$$

The water must act through its active constituents, the hydrogen and hydroxyl ions, and these will add to the double bond between the carbon and nitrogen atoms, as in many well-proved organic reactions,



$$C_6H_5C(:\overset{+}{N}H_2)OCH_3 + \overset{+}{H} + \overset{-}{OH} \rightleftharpoons C_6H_5C\left\{\begin{matrix}\overset{+}{N}H_3\\ OH\\ OCH_3\end{matrix}\right. \quad (55).$$

It must be the product of this action, the addition product formed, which ultimately suffers the decomposition in question,



$$C_6H_5C\left\{\begin{matrix}\overset{+}{N}H_3\\ OH\\ OCH_3\end{matrix}\right. \rightleftharpoons C_6H_5COOCH_3 + \overset{+}{N}H_4 \quad (56).$$

By considering (55) and (56) we find that hydrochloric acid would increase the concentration of the positive ion in both equations, and that its accelerating action may ultimately be due, then, to either or both of these causes: to the reactivity or additive power towards water of the positive ion $C_6H_5C(:\overset{+}{N}H_2)OCH_3$, whose mass is increased (55); or to the instability, as given in (56), of the ion addition product $C_6H_5C(\overset{+}{N}H_3)(OH)OCH_3$, whose mass is also increased. It is, as yet, impossible to distinguish experimentally between these two possibilities, but on the basis of what follows we consider that it is most likely the instability of the addition product which is the ultimate cause of the action and of the accelerating effect of the hydrochloric acid.

It is characteristic that the result is the acceleration of a reaction according to which from one positive ion (the imidoester ion) is formed the positive ion (NH_4) of another base, ammonium hydroxide, which is much *stronger* than the original base, the imidoester. By comparing the reaction velocities and the affinity constants of analogous imidoesters, we have found, in fact, that the reaction velocities for closely related bases are greatest for the weakest bases.[1]

For instance, methyl imido-*m*-nitrobenzoate is a much weaker base than methyl imidobenzoate and its salt is decomposed very much faster than that of the latter. It will be observed that the weaker and less stable base is derived from the stronger acid, a fact which is of interest in connection with a similar observation by Euler[2] that the esters of the stronger acids are decomposed more rapidly by water than are those of the weaker acids. Here again we have a perfect parallelism between the imidoesters and the ordinary esters, only in the case of the former we have been able to obtain all the essential factors by experimental measurements.

If we apply the conclusions as to the mechanism of the decomposition of the imidoesters by water to the problems of esterification and saponification, we obtain the following as representing the course of the reactions, referred to the structures of the active substances. Since, as was shown in Part IV., the decomposition of an ester by water in the presence of an acid is due to the action of the active constituents of water on the positive oxonium ion of the ester, we have

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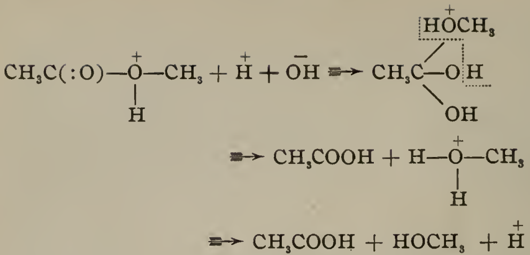
[1] **Full details on this point are contained in the article by Dr. McCracken.**

[2] ***Loc. cit.***

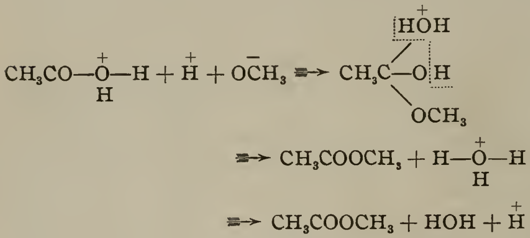


$$\mathrm{CH_3C(:O){-}\underset{\displaystyle |\atop \displaystyle H}{\overset{+}{O}}{-}CH_3} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{OH}} \rightarrow \mathrm{CH_3C{\cdots}} \qquad (57),$$

$$\rightarrow \mathrm{CH_3COOH} + \mathrm{H{-}\underset{\displaystyle |\atop \displaystyle H}{\overset{+}{O}}{-}CH_3} \qquad (58),$$

$$\rightarrow \mathrm{CH_3COOH} + \mathrm{HOCH_3} + \overset{+}{\mathrm{H}} \qquad (59).$$

Again we note the tendency of one positive ion, the ester oxonium ion, to lose the positive ion of an undoubtedly stronger base, the oxonium ion of methyl alcohol; and *the same is true for the reversed reaction*, that of esterification, for which we have



$$\mathrm{CH_3CO{-}\underset{\displaystyle H}{\overset{+}{O}}{-}H} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{OCH_3}} \rightarrow \mathrm{CH_3C{\cdots}} \qquad (60),$$

$$\rightarrow \mathrm{CH_3COOCH_3} + \mathrm{H{-}\underset{\displaystyle H}{\overset{+}{O}}{-}H} \qquad (61),$$

$$\rightarrow \mathrm{CH_3COOCH_3} + \mathrm{HOH} + \overset{+}{\mathrm{H}} \qquad (62).$$

The oxonium ion of water, $\overset{+}{\mathrm{H_3O}}$, is formed first and there can be no question, although we are dealing with minimally small constants,[1] that water must form a much stronger oxonium base than does acetic acid.

It appears, then, that in the presence of acids there is a general tendency toward the formation of the positive ions of the strongest bases[2]—representing, most likely, the greatest decrease of free energy in a given system. This conclusion has found a further confirmation in our most recent observations on the action of ammonia on imidoesters; the action proceeds quantitatively according to

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[1] The experimental determination of these and similar minimally small constants in organic chemistry undoubtedly will clear up most of the mysteries connected with organic reactions, just as the minute but exact constants for the instability of the complex ions, as determined by Bodlaender. Euler, and others, and the immense range of the constants of solution tensions have thrown wonderful light on many complex inorganic reactions which now appear as simple results of the fulfillment of definite, although often inconceivably large or minute, natural constants.

[2] In the presence of alkalis, we have, *vice versa*, a universal tendency towards the formation of strongest acids, *i. e.*, towards neutralization.

$$RC(:\overset{+}{N}H_2)OR' + NH_3 \rightarrow RC(:\overset{+}{N}H_2)NH_2 + HOR' \quad (63),$$

amidine ions being formed in a reaction with a very large velocity constant, rather than ammonium ions and an acid ester; of all the bases whose salts could be formed, the amidines are strongest.[1]

On the other hand, salts of the isoureas, which belong to the class of imidoesters, are remarkably stable toward water; they are not decomposed, even by hot water, into ammonium ions and ester; the action

$$NH_2C(:\overset{+}{N}H_2)OR + HOH \rightarrow NH_2COOR + \overset{+}{N}H_4 \quad (64)$$

does not take place,[2] as is the case for all other imidoesters. In this case where the decomposition does not take place, we have the significant fact that the affinity constant of the original base,[3] the isoureaester, is 6.4×10^{-5}, which is larger than that of ammonium hydroxide (1.8×10^{-5}), the base whose ion, NH_4, would be formed by a hydrolytic decomposition.[4]

V. Summary.

The results reported in this paper may be summarized as follows: (1) The catalytic action of acids has been proved to be due to the production of salts whose ions form the active mass in the reactions accelerated by acids. This has been proved quantitatively by measurements made with a large number of imidoesters. It has been confirmed by quantitative studies of the action of ammonia on imidoesters, the velocity of this action being proportionate to the concentration of the positive imidoester ion, although the latter forms a component only to an extent which is minute but rigorously calculable. When the action is retarded by the presence of an acid, the reacting component is the free, molecular base, and the retardation (negative acceleration) is again simply due to salt and ion formation.

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[1] Miss Blunt will report in detail on this work, a preliminary report of which was read in December, 1906, at the meeting of the American Chemical Society.

[2] Stieglitz and McKee: THIS JOURNAL, **26**, 209 (1901).

[3] Bruce: J. Am. Chem. Soc., **26**, 419 (1904).

[4] In a later paper this question will be treated more fully on the basis of our most recent results, which, it may be said, agree perfectly with the above principle.

(2) The rigorous application of the above principle to the catalysis of esters and to the process of esterification leads, with the aid of the laws of equilibrium and without any further assumptions, directly to all the fundamental equations expressing the course of such a catalysis or esterification, as well as to the fundamental equation expressing the condition of equilibrium arrived at in the reversible process.

(3) The same conception applied to catalytic actions by alkalis leads to the principle that their effect is due to the formation of salts whose negative ions form the active mass in the action.

(4) In reactions which are accelerated in acid solution there is the tendency to form positive ions of a base stronger than the original base undergoing decomposition.

(5) In accordance with the results, our views concerning catalytic action[1] must be modified in regard to all three of the commonly assumed fundamental characteristics of catalytic action, *viz.*, (1) that the acceleration must be proportionate to the concentration of the catalytic agent present; (2) that the agent must not appear to combine with any of the substances undergoing change; and (3) that the ultimate condition of equilibrium must not be measurably modified by the presence of a catalyzer. These characteristics are practically true only for limiting cases where the amount of salt formation is so small as to be beyond

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[1] Reference should be made to Euler's papers on catalytic action, Z. physik. Chem., **36**, 641 (1901), and **47**, 353 (1904), in which the acceleration in the catalysis of methyl acetate, etc., is also explained on the basis of an assumed ionization of the organic compounds. How little the mere idea of ionization without the safe basis of experimental confirmation and measurements and without the application of the experience of organic chemistry can be relied upon to develop the subject from a purely mathematical standpoint is evident from the impossible reactions and forms of ionization of organic compounds which are assumed in a number of cases in the first, main paper. In the second, brief paper on the inversion of cane sugar, salt formation (as a carbonium salt) and hydrolysis is assumed somewhat as in this paper, but without experimental confirmation. It may be said that the work published here was already completed at the time this second paper of Euler's appeared and was reported during the same summer at the St. Louis Congress of Arts and Science (see page 29).

the scope of our measurements. None of them is absolutely true under any conditions. When the amount of salt formation becomes measurable, as for imidoesters, they need not hold even approximately, and *still the fundamental mechanism and mode of the catalysis is the same in these cases* as in the others. The one vital fact, then, of an acceleration due to an increase in the active mass or concentration of a reacting component in a catalytic action is the only fundamental fact common to all catalytic actions. Only for a special, but important and interesting, class of actions, the above principles hold as a very close approximation which can be derived, by the ordinary laws of chemical equilibrium, as a mathematical necessity from the fundamental principle laid down.[1]

Work is being continued along all of the above lines and will include also the study of the formation of acid amides by the action of ammonia on acid esters; the measurement, quantitatively, of the combination of acids with ordinary esters in their catalysis; and the quantitative effect of an added acid in the condition of equilibrium between acid, alcohol, ester, and water; the reactions of the acid nitriles in the presence of acids; and the study of the "Beckmann rearrangement" as an ionic reaction.

This statement has become necessary in consequence of an invasion of our field of work by another investigator.

ON PHENYLMALONIC NITRILE.

[SECOND PAPER.]

BY JOHN C. HESSLER.

In a preliminary paper,[2] the writer described the preparation of phenylmalonic nitrile and the attempt to prepare its silver salt. This salt could not be isolated because of its instability, but there was obtained from it a substance, melting at 147° to 148°, which was analyzed. This substance turns out to be only one of several products formed by the spontaneous decomposition of the silver salt; a further study of these products is contained in the present paper. There is added, also, a description of several new derivatives of phenylcyanacetic ether and of phenylmalonic nitrile.

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[1] The following studies on catalysis will shortly be published from this laboratory, the experimental work having already been completed:

Catalytic Reactions with Imidoesters, by J. Stieglitz.
The Catalysis of Imidoesters by Acids, by Ira H. Derby.
The Catalysis of Imidoesters, by Wm. McCracken.
The Catalysis of Imidoesters, by Hermann Schlesinger.
The Catalysis of Imidoesters as Affected by the Presence of Nonelectrolytes and Electrolytes, by Edith E. Barnard.
The Formation of Amidines, by Katharine Blunt.
The Action of Ammonia on Isoureaesters, by Robert A. Hall.
The Rearrangement of *o*-Aminophenylesters, by Louis A. Test.

[2] THIS JOURNAL, **32**, 119.

Silver Salt of Phenylmalonic Nitrile.

Twenty grams of phenylmalonic nitrile were converted, as previously described,[1] into the silver salt. This was dried over night on a clay plate. A sample dried *in vacuo* over sulphuric acid and then ignited gave 44.27 per cent of silver. Calculated for $C_9H_5N_2Ag$, 43.37 per cent. The remainder of the salt was extracted eight times with boiling ether. The organic material extracted by the ether was left, after the solvent had been distilled, as a pasty, white mass. The insoluble residue weighed 17.2 grams when dried on a clay plate.

When the organic material extracted by ether was treated again with cold ether, all except a small amount (0.2 to 0.3 gram) dissolved. This insoluble portion was filtered off and dried on a clay plate; it melted with decomposition at 210° to 215°.

The ether filtrate was concentrated to 250 cc., an equal volume of ligroin (boiling at 40° to 60°) was added, and the mixture was left in a room at winter temperature for two days. There was obtained a white, pasty precipitate which weighed about 3 grams. It was filtered off, and the ether-ligroin solution was then concentrated to 250 cc. and allowed to cool. An almost colorless oil separated out; after some hours this solidified to almost colorless crystals which melted at 87° to 88° after being dried on a clay plate. By successive concentrations of the ether-ligroin mother liquor and by addition of some of the crystals first obtained to the oil which separated out, there were collected in all 7.7 grams of the solid melting at 87° to 88°.

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[1] This Journal, **32**, 125.

The pasty precipitate mentioned above (weight, about 3 grams) was treated with ether; only 0.35 gram remained insoluble; this melted at 210° to 220° with decomposition. The ether filtrate was treated with ligroin (40° to 60°) and gave 0.9 gram of the apparently amorphous powder melting at 147° to 148°. The filtrate from this, after being concentrated, gave a further small amount of the crystals melting at 87° to 88°.

It is evident, therefore, that at least *three* organic substances result when the silver salt of phenylmalonic nitrile is decomposed; these melt at 87° to 88°, at 147° to 148°, and at approximately 210° to 220°, respectively.

Dimolecular Phenylmalonic Nitrile.

A. *Analysis.*—The body melting at 87° to 88° was recrystallized from ether-ligroin and dried *in vacuo* over sulphuric acid.

I. 0.2057 gram substance gave 0.5707 gram CO_2 and 0.0689 gram H_2O.

II. 0.1502 gram substance gave 0.42 gram CO_2 and 0.0552 gram H_2O.

III. 0.1272 gram substance gave 22.3 cc. N at 20° C. and 747 mm.

	Calculated for $(C_9H_6N_2)_2$.	Found. I.	 II.	 III.
C	76.06	75.67	76.26	. .
H	4.22	3.72	4.08	. .
N	19.72	. .	. .	19.8

The substance is burned with great difficulty. In combustion II. it was mixed with cupric oxide in wire form; in the others, powdered cupric oxide was used. The last portions of nitrogen came off only at bright red heat.

B. *Molecular Weight.*—Molecular weight determinations of the body melting at 87° to 88°, made by the boiling point method, agree fairly well with the dimolecular formula $(C_9H_6N_2)_2$. The apparatus was that of McCoy;[1] the solvents used were benzene and absolute alcohol.

a. In Benzene Solution (constant = 3280).—1.0171 grams substance caused a rise of 0.31° C. in the boiling point of the solution when its volume was 32.5 cc., and of 0.303° C. when the volume was 34.8 cc.

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[1] This Journal, 23, 353–360.

	Calculated for $(C_9H_6N_2)_2$.	Found. I.	Found. II.
Mol. wt.	284	331	316

b. In Alcoholic Solution (constant = 1560).—1.3372 grams substance caused a rise of 0.203° C. when the volume of the solution was 33.6 cc., and of 0.188° when the volume was 35.2 cc.

	Calculated for $(C_9H_6N_2)_2$.	Found. I.	Found. II.
Mol. wt.	284	306	315

C. *Properties.*—Dimolecular phenylmalonic nitrile dissolves readily in alcohol and ether. Water precipitates it from alcoholic solution as an oily liquid which soon crystallizes in hard granules melting at 87° to 88°. From benzene solution the substance did not crystallize readily. The solution was therefore treated with an equal volume of ligroin (40° to 60°) and allowed to stand overnight. The substance then crystallized in large, white plates which melted at 67° to 68° after they had been dried for five minutes on a clay plate. When the crystals were left in the air they shrank together and became very sticky; at the same time benzene was given off. A determination of the combined benzene gave the following result:

1.0202 grams substance (dried five minutes on a clay plate) were left *in vacuo* over sulphuric acid until no further loss of weight took place (50 days). The total loss of benzene was 0.2164 gram.

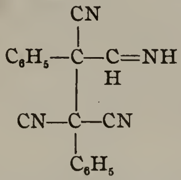
	Calculated for $(C_9H_6N_2)_2.C_6H_6$.	Found.
C_6H_6	21.55	21.21

The residue of dimolecular phenylmalonic nitrile melted sharply at 87° to 88°. Heated on a nickel spatula the substance is decomposed, giving off pungent, red vapors. It dissolves readily in caustic soda solution to form the sodium salt. The amount of alkali required indicates that the dimolecular nitrile is monobasic; one gram of it was just dissolved by 3.5 cc. of normal sodium hydroxide solution.

An absolute ether solution of the nitrile was treated with sodium in the form of chips. After two weeks the sodium had been converted into the yellow sodium salt; this was insoluble in ether but readily soluble in water.

The solution obtained from the nitrile and the theoretical amount of normal sodium hydroxide gave, when poured into silver nitrate solution, a white precipitate of the silver salt (*q. v.*).

A possible formula for the dimolecular nitrile, based upon its known properties, is this:



The hydrogen of the imine group would thus be the ionic hydrogen.

Trimolecular Phenylmalonic Nitrile.

The analysis of the substance melting at 147° to 148° was reported in the preliminary paper (*q. v.*). A molecular weight determination by the method of McCoy gave results indicating that the substance is probably trimolecular phenylmalonic nitrile.

0.7599 gram substance, in benzene solution, caused a rise of 0.165° C. in the boiling point when the volume of the solution was 32.6 cc.

Calculated for $(C_9H_6N_2)_3$.	Found.
426	463

Oxidation of Phenylmalonic Nitrile and Its Polymers by Means of Chromic Acid.

Phenylmalonic nitrile and both its polymers give *the same substance* when oxidized with chromic acid in glacial acetic acid solution. The product is an amorphous solid melting at 210° to 230° with decomposition, and gives, when analyzed, values agreeing with the formula $(C_9H_5N_2)._x$ On this account it seems probable that the oxidation of each $C_9H_6N_2$ molecule (or group) results in the loss of one atom of hydrogen. The behavior of the sodium salt of phenylmalonic nitrile with bromine (*q. v.*) makes this still more likely.

A. *Oxidation of Phenylmalonic Nitrile.*—Phenylmalonic nitrile (0.5 gram), specially purified by recrystallization from dilute alcohol, was dissolved in 10 cc. of glacial acetic acid and treated with chromic acid in the same solvent. The chromic acid solution was added drop by drop; the color of the first few drops was changed in a few seconds to bright green, and at the same time an amorphous, white solid was precipitated. Altogether, 0.5 gram of chromic acid was added. The amount theoretically necessary to give one atom of oxygen for every two molecules of the nitrile ($C_9H_6N_2$) is 0.12 gram. The mixture was allowed to stand overnight. Water was added to precipitate the oxidation product, which was filtered off, washed with water, and dried on a clay plate and *in vacuo* over sulphuric acid. The substance melted at 215° to 230° with decomposition.[1]

0.1426 gram substance gave 0.3997 gram CO_2 and 0.0492 gram H_2O.

	Calculated for $(C_9H_5N_2)_x$.	Found.
C	76.59	76.43
H	3.55	3.83

B. *Oxidation of Dimolecular Phenylmalonic Nitrile by Chromic Acid.*—Five-tenths of a gram of the dimolecular nitrile, $(C_9H_6N_2)_2$, was dissolved in glacial acetic acid and treated with an excess of chromic acid dissolved in the same solvent. As in the case of phenylmalonic nitrile, the chromic acid was reduced and a white solid was precipitated. The precipitate was washed with water and dried on a clay plate and *in vacuo* over sulphuric acid. It weighed 0.5 gram. When heated in a melting point tube at 215° to 230°, it is decomposed.

0.1573 gram gave 0.4418 gram CO_2 and 0.0532 gram H_2O.

	Calculated for $(C_9H_5N_2)_x$.	Found.
C	76.59	76.61
H	3.55	3.76

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[1] A special experiment with benzylmalonic nitrile (This Journal, **22**, 180) showed that this substance is not oxidized by chromic acid in glacial acetic acid solution.

C. *Oxidation of Trimolecular Phenylmalonic Nitrile.*—The trimolecular nitrile, melting point 147° to 148°, gave, when treated with chromic acid in acetic acid solution, an amorphous white solid having exactly the same properties as the substance obtained from phenylmalonic nitrile and from the dimolecular body.

It will be noticed that a small amount of a substance having approximately the same properties was obtained from the products formed by the decomposition of the silver salt of phenylmalonic nitrile. It was difficultly soluble in ether and melted with decomposition at 210° to 215°. This must have been formed by the oxidation of phenylmalonic nitrile or of its polymers by means of silver oxide.

Action of Sodium Phenylmalonic Nitrile with Bromine.—The sodium salt of phenylmalonic nitrile was subjected to the action of bromine in the expectation that phenylbrommalonic nitrile would be produced, but the chief product seems to be the amorphous solid melting with decomposition at 215° to 230° which was produced by the oxidation with chromic acid.

A. *Addition of Bromine to the Sodium Salt.*—To 3 grams of sodium phenylmalonic nitrile, suspended in 30 cc. of chloroform, there was added, drop by drop, a solution of bromine in chloroform. One atomic weight of bromine was used for every molecular weight of the sodium salt. A white precipitate of sodium bromide separated out. It was filtered off, dried, and weighed. 1.5 grams were obtained instead of 1.9 grams, the theoretical amount. The chloroform solution, when distilled on a water bath, left an oily liquid which was difficultly soluble in ether. It was redissolved in chloroform and precipitated by ligroin; 0.9 gram of an amorphous, white solid was obtained. A second reprecipitation from chloroform solution by means of ligroin yielded 0.45 gram of the substance. It shrank together at 210° to 220° and melted to a black tar at 230°. It was dried *in vacuo* over sulphuric acid and analyzed.

I. 0.1473 gram substance gave 0.4097 gram CO_2 and 0.0489 gram H_2O.

II. 0.1153 gram substance gave 19.8 cc. N at 19.5° C. and 742.8 mm.

	Calculated for $(C_9H_5N_2)_x$.	Found.
C	76.59	75.86
H	3.55	3.69
N	19.86	19.32

The substance is burned with difficulty. Possibly it contains a trace of bromine. Its formation probably takes place according to the equation

$$xC_9H_5N_2Na + xBr \rightarrow (C_9H_5N_2)_x + xNaBr.$$

B. *Addition of Sodium Phenylmalonic Nitrile to Bromine* (two atoms).—Two and eight-tenths grams of sodium phenylmalonic nitrile were added in portions of 0.1 gram each to a solution of 3 grams of bromine in 40 cc. of chloroform. The temperature rose to 35°, a large excess of bromine remained, and a white precipitate of sodium bromide appeared. The mixture was treated with water in a separatory funnel and the chloroform solution was dried with calcium chloride and then distilled. When about four-fifths of the chloroform and the excess of bromine had been removed, a white, crystalline solid separated out. This was filtered off and found to weigh 0.35 gram. It melted at 117°. The substance is soluble in chloroform, difficultly soluble in alcohol, and insoluble in ligroin (40° to 60°). It crystallized from benzene in small granules melting at 118°. The substance was at first supposed to be phenylbrommalonic nitrile but it was later shown that no bromine was present.

0.1051 gram substance gave 0.2958 gram CO_2 and 0.0399 gram H_2O.

	Calculated for		Found.
	$(C_9H_6N_2)_x$.	$(C_9H_5N_2)_x$.	
C	76.06	76.59	76.75
H	4.22	3.55	4.21

The small amount of the substance available has prevented its further investigation up to the present time. The filtrate from the crystals melting at 117° gave gummy substances when concentrated; there was also obtained 0.15 gram of the amorphous solid melting with decomposition at 215° to 230°.

C. *Addition of Sodium Phenylmalonic Nitrile to Bromine* (one atom).—Three and eight-tenths grams of sodium phenylmalonic nitrile were added in 0.2 gram portions to a solution of 1.9 grams (one atom) of bromine in 50 cc. of chloroform. All the bromine reacted. The sodium bromide was filtered off and the filtrate was distilled. Not a trace of the solid melting at 117° was obtained, but only a thick gum which gave, when treated with ether, 1.7 grams of the white solid melting at 210° to 230°. A repetition of this experiment with a slight excess of bromine gave only traces of the solid melting at 117°; the chief product is the amorphous substance decomposing at 210° to 230°.

The Silver Salt of Dimolecular Phenylmalonic Nitrile.

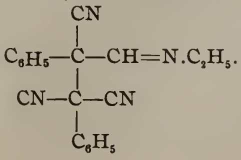
It has already been stated that when the sodium salt of dimolecular phenylmalonic nitrile is added to a solution of silver nitrate the silver salt is precipitated. One gram of the nitrile was dissolved in the theoretical amount, 3.5 cc., of normal sodium hydroxide solution and the resulting solution of the sodium salt added to an excess of silver nitrate solution. The precipitate was almost pure white and did not become dark when filtered. It changed color, however, when dried on a clay plate. It was dried *in vacuo* over sulphuric acid until its weight was constant. The amount obtained was considerably over one gram.

0.2433 gram substance gave, on ignition, 0.0669 gram Ag.

	Calculated for $C_{18}H_{11}N_4Ag$.	Found.
Ag	27.62	27.49

The dark colored silver salt was extracted with ether, but only a trace went into solution; the salt is not, therefore, decomposed appreciably at the ordinary temperature. It is decomposed, however, when heated on a water bath at 90°.

Ethyl Dimolecular Phenylmalonic Nitrile,



$$\begin{array}{c} \mathrm{CN} \\ | \\ \mathrm{C_6H_5-C-CH{=}N.C_2H_5.} \\ | \\ \mathrm{CN-C-CN} \\ | \\ \mathrm{C_6H_5} \end{array}$$

—When one gram of the silver salt of dimolecular phenylmalonic nitrile was added to 4 grams of ethyl iodide (theory, 1.56 grams), the two substances reacted with a hissing noise and the mixture became decidedly warm. After standing one hour the mixture was heated to 80°, cooled, and filtered. The silver iodide weighed 0.5 gram. The filtrate was distilled *in vacuo* and 0.6 gram (theory, 0.8 gram) of a slightly colored, gummy residue was obtained. This was dissolved in ether and the solution was treated with ligroin (40° to 60°). After two days there was obtained a crop of crystalline plates grouped in rosettes. These melted at 101° to 102° after being dried *in vacuo* over sulphuric acid.

0.1442 gram substance gave 22.8 cc. N at 22° C. and 744.5 mm.

	Calculated for $C_{20}H_{16}N_4$.	Found.
N	17.95	17.63

n-Butyl Dimolecular Phenylmalonic Nitrile,

$C_9H_6N_2.C_9H_5N_2.C_4H_9$.

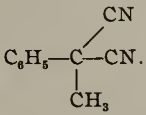
—One and a half grams of the silver salt were added to 7.5 grams of *n*-butyl iodide. As with ethyl iodide, the temperature rose to 40°. The mixture was allowed to stand a week; a faint odor of isocyanide was noticed. Ether was then added, the silver iodide filtered off, and the filtrate distilled up to 70° *in vacuo* (20 mm.). The residue was a slightly colored, thick gum and weighed 1.25 grams, practically the theoretical amount. The gum was dissolved in ether, treated with ligroin (40° to 60°) until the ether solution began to be turbid, and allowed to stand for a week in the cold. Large, crystalline plates were thus obtained which were aggregated in rosettes. The melting point of the crude substance was 79° to 80°. After the body had been washed with ether it was perfectly white and melted at 80° to 81°.

0.1548 gram gave 23.5 cc. N at 27° and 745.4 mm.

	Calculated for $C_{22}H_{20}N_4$.	Found.
N	16.47	16.54

Both the ethyl and the *n*-butyl bodies gave off their nitrogen very slowly; the last portions only at a bright red heat.

Methylphenylmalonic Nitrile,



$$C_6H_5—C(CN)(CH_3)—CN.$$

—Three grams of sodium phenylmalonic nitrile were treated with 12 grams (the theoretical amount is 2.6 grams) of methyl iodide. Since there was no apparent action at the ordinary temperature the mixture was heated in a sealed tube for 9 hours. The product was treated with water and extracted with ether; the ether solution was then washed with 10 per cent sodium hydroxide solution, dried with calcium chloride, and distilled on a water bath. There remained an oily substance which was distilled at 125° to 130° under 16 mm. pressure. Yield, 1.8 grams.

I. 0.1708 gram substance gave 0.4797 gram CO_2 and 0.0837 gram H_2O.

II. 0.1178 gram substance gave 19.4 cc. N at 23° C. and 748.1 mm.

	Calculated for $C_{10}H_8N_2$.	Found. I.	II.
C	76.92	76.60	. .
H	5.13	5.44	. .
N	17.95	. .	18.36

Attempts to get the substance in solid form were not successful.

Action of Sodium Phenylmalonic Nitrile with Benzenediazonium Chloride.

Phenylmalonic nitrile (3.5 grams), dissolved in 20 cc. of absolute alcohol, was treated with 0.57 gram (one atomic equivalent) of sodium, and the resulting solution of the sodium salt was added in small portions to an ice-cold, aqueous solution containing one molecular equivalent of benzenediazonium chloride. The precipitate that separated out was oily at first, but it soon solidified and was almost white. The solution became red and then dark blue. The blue color persisted several days. The substance which produced it could be extracted with ether; dilution with water caused it to disappear, while addition of absolute alcohol restored it. The resulting diazonium body was dried on a clay plate for 45 minutes. It weighed 4.2 grams. A portion that was left in a moist condition upon a funnel exploded. The dried substance was also decomposed with a slight explosion when warmed. When it was treated with ether, the substance gave off nitrogen.

Two grams of the dried diazonium body were added to 25 cc. of ether in a flask connected with an azotometer, the gas evolved being first passed through a wash bottle of alcohol. The theoretical amount of nitrogen capable of being produced from the benzenediazonium group is about 180 cc. under standard conditions; the amount actually collected was 82 cc., measured under ordinary conditions of temperature and pressure, but as the evolution of gas went on even in the absence of ether much nitrogen had undoubtedly been given off in the process of drying.

During the evolution of the nitrogen a white solid was precipitated; this weighed 0.2 gram after it had been dried on a clay plate, and melted at 107°. The ether solution gave, on evaporation, a thick, tarry liquid which solidified, in part, *in vacuo*. It has not been examined further.

An analysis of the solid melting at 107° showed that it was either another polymeric phenylmalonic nitrile or a substance of the formula $(C_9H_5N_2)_x$.

0.1396 gram substance gave 0.3928 gram CO_2 and 0.0505 gram H_2O.

	Calculated for		
	$(C_9H_6N_2)_x$.	$(C_9H_5N_2)_x$.	Found.
C	76.06	76.59	76.72
H	4.22	3.55	4.02

Action of Phenylcyanacetic Ether with Ammonium Hydroxide (repeated); *Phenylcyanacetamide.*

The preparation of phenylcyanacetamide, already described in the preliminary paper, has been repeated with the following results:

Forty grams of phenylcyanacetic ether, boiling at 160° to 170° under 18 mm. pressure, were treated with 70 grams of concentrated, chemically pure ammonium hydroxide (sp. gr. 0.90). The ester dissolved at once. A large amount of the amide separated out in 15 minutes when the solution was treated with a crystal of the same substance. After 5 hours the crystals were filtered off and dried on a clay plate. They weighed 23.7 grams. Water was added to the ammoniacal filtrate and the diluted solution allowed to stand overnight. In this way 2.6 grams more of the amide were obtained, making a total of 26.3 grams, or 80 per cent of the theoretical amount.

When the ammoniacal solution was acidified with dilute sulphuric acid and extracted with ether, there were obtained 3.8 grams of phenylcyanacetic acid. When this was recrystallized from 12 grams of benzene, 2.7 grams were obtained, which melted at 93° to 94° after being dried over sulphuric acid *in vacuo*.

Twenty-seven grams of the amide gave, when crystallized from 150 cc. absolute alcohol, 21.6 grams of six-sided prisms.

Action of Phenylcyanacetic Ether with Aniline, with the Toluidines, and with Phenylhydrazine.

1. *Phenylcyanacetanilide.*—Two grams of the ester and 2 grams (twice the theoretical amount) of aniline were heated over a free flame until alcohol distilled off. The residue was a thick gum which solidified when cold. It was treated with ether, filtered off, and dried on a clay plate. There were obtained 1.9 grams of phenylcyanacetanilide. When crystallized from absolute alcohol, it separated out in grouped needles melting at 136°. The anilide is only slightly soluble in ether and practically insoluble in water. Analysis gave the following results:

I. 0.1562 gram substance gave 0.4358 gram CO_2 and 0.0739 gram H_2O.

II. 0.1848 gram substance gave 19.4 cc. N at 19° C. and 747.3 mm.

	Calculated for $C_{15}H_{12}ON_2$.	Found. I.	Found. II.
C	76.27	76.09	. .
H	5.08	5.26	. .
N	11.87	. .	11.91

2. Phenylcyanacetic Acid Toluidides.—Phenylcyanacetic ether and *p*-toluidine were heated until no more ethyl alcohol distilled off. The residual liquid crystallized when cold. When recrystallized from absolute alcohol the *p*-toluidide separated out in long needles melting at 139°. The ortho- and meta-toluidides were made in the same way; the ortho body melted at 139° and the meta compound at 131°. All the toluidides are more easily soluble in ether than the anilide. All are difficultly soluble in water.

3. Phenylcyanacetic Acid Phenylhydrazide.—Three and three-tenths grams of the ester and 2 grams (the theoretical amount) of phenylhydrazine were heated to 150° to 200° in a metal bath until no more alcohol could be distilled off. The crude phenylhydrazide melted at 207°.

The same substance was formed when phenylcyanacetic ether was allowed to stand several days with an excess of phenylhydrazine.

The phenylhydrazide is soluble in about 30 parts of boiling absolute alcohol and crystallizes from the alcoholic solution in large, hard granules melting at 224°. It is difficultly soluble in ether and insoluble in water. It was recrystallized from alcohol for analysis.

0.1447 gram substance gave 22.5 cc. N at 26.5° C. and 743.8 mm.

	Calculated for $C_{15}H_{13}ON_3$.	Found.
N	16.73	16.94

Action of Sodium upon Carbonic Acid Ethyl Ester and Malonic Nitrile.

Two grams of sodium in wire form were added to 10 grams of carbonic ether and 5.6 grams of malonic nitrile, dissolved in 200 cc. of absolute ether. The reaction was a slow one, but after a week the sodium had disappeared. The sodium salt was filtered off and dried over sulphuric acid *in vacuo*. Yield, 7.5 grams. Analysis showed that the substance was sodium malonic nitrile.

0.4239 gram substance gave 0.3376 gram Na_2SO_4.

	Calculated for $CHNa(CN)_2$.	Found.
Na	26.13	25.76

Action of Hydrochloric Acid upon an Alcoholic Solution of Phenylmalonic Nitrile.

Two grams of phenylmalonic nitrile dissolved in 20 cc. of absolute alcohol were treated with 20 cc. concentrated, chemically pure hydrochloric acid of specific gravity 1.2. Ammonium chloride crystallized out in a few hours; after three days it was filtered off and the filtrate was distilled *in vacuo* up to 55°. The residue contained more ammonium chloride; this was removed by treatment with absolute alcohol. Altogether, 0.55 to 0.6 gram of ammonium chloride was obtained.

The absolute alcohol was then removed *in vacuo* and the residue was treated with water and extracted with ether. The ether solution was separated into (*a*) a portion soluble in 10 per cent sodium carbonate and (*b*) a portion neutral to sodium carbonate.

(*a*) The sodium carbonate solution was acidified with dilute sulphuric acid and extracted with ether, and the ether solution dried with calcium chloride. Distillation of the ether left about 0.2 gram of an oily liquid which solidified *in vacuo* over sulphuric acid. Its properties were those of phenylcyanacetic acid; it melted at 90° to 92° when crystallized from benzene and was decomposed at 140° to 165° with evolution of carbon dioxide.

(*b*) The ether solution containing the substances neutral to sodium carbonate was distilled on a water bath. There remained an oily liquid which consisted chiefly of phenylcyanacetic ether and phenylcyanacetamide. When it was treated with ether about 0.1 gram of the amide remained as white crystals melting at 147° to 148°. The ether solution gave 1.35 grams of pure phenylcyanacetic ether boiling at 161° to 162° under 16 mm. pressure. It was treated with concentrated ammonia water and thus converted into the pure amide melting at 149° to 150°.

Phenylcyanpyroracemic Acid Ethyl Ester.

Since W. Wislicenus was able to prepare phenylmalonic ether by splitting off carbon monoxide from phenyloxalacetic ether,[1]

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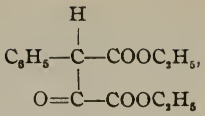
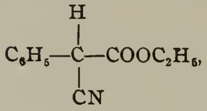
[1] Ber. d. chem. Ges., **20**, 593; **27**, 1091.



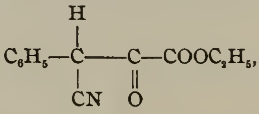
$$\begin{array}{rcl} & H & \\ & | & \\ C_6H_5- & C & -COOC_2H_5, \\ & | & \\ O= & C & -COOC_2H_5 \end{array}$$

the writer hoped to be able to prepare *phenylcyanacetic ether*,



$$\begin{array}{rcl} & H & \\ & | & \\ C_6H_5- & C & -COOC_2H_5, \\ & | & \\ & CN & \end{array}$$

from *phenylcyanpyroracemic acid ethyl ester*,



$$\begin{array}{rcccl} & H & & & \\ & | & & & \\ C_6H_5- & C & \text{——} & C & -COOC_2H_5, \\ & | & & \| & \\ & CN & & O & \end{array}$$

by a similar reaction. The attempt was not successful, but the results of the experiments are given. Erlenmeyer, jun., prepared phenylcyanpyroracemic ether from benzyl cyanide, oxalic ether, and sodium.[1] His method was repeated, as follows:

Twenty-five grams of oxalic ether and 21 grams of benzyl cyanide (practically molecular quantities) were dissolved in 100 cc. of absolute ether and treated with 4 grams (one atomic equivalent) of sodium in wire form. The reaction was noticeable only after about one hour and was controlled by means of running water. After the sodium had disappeared the product of the reaction was allowed to stand for 24 hours. The sodium salt had then separated out. Water and dilute sulphuric acid were added and the solid ester, together with some unchanged benzyl cyanide and oxalic ether, was extracted with ether. Twenty-seven grams of the crude substance were obtained. It could be recrystallized from hot water and from ether-ligroin. When purified it melted at 129° to 130°. An analysis gave the following result:

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[1] Ann. Chem. (Liebig), **271**, 172.

0.2096 gram substance gave 0.5108 gram CO_2 and 0.0986 gram H_2O.

	Calculated for $C_{12}H_{11}O_3N$.	Found.
C	66.36	66.46
H	5.07	5.23

Phenylcyanpyroracemic acid ethyl ester is readily soluble in alcohol, chloroform, and ether. It is distilled without decomposition at 206° under 20 mm. pressure. Ten per cent caustic soda extracts it from ether solution. Concentrated ammonia water dissolves it, giving, after some hours, oxamide and benzyl cyanide in practically theoretical amounts. It is soluble, also, in aqueous sodium carbonate, and is precipitated from the solution by dilute sulphuric acid.

Effect of Heat upon Phenylcyanpyroracemic Acid Ethyl Ester.

Four and six-tenths grams of the ester were heated at 230° to 240° in a distilling flask connected with a receiver and an azotometer. The volume of gas collected was 300 cc. It burned like carbon monoxide, and the last 100 cc. were completely absorbed by ammoniacal cuprous chloride. On raising the temperature to 300°–350° about 2 cc. of a liquid distilled over into the receiver. This boiled at 100° to 140° at 15 mm.

A similar result was obtained when the ester was heated to 240°–250° under ordinary pressure until the carbon monoxide had been driven off and the residue was then heated *in vacuo* (15 mm.). The substance sought was not formed in appreciable quantity.

Decomposition of the Ester by Aqueous Sulphuric Acid.

An ether solution of the crude ester was shaken three times with 10 per cent sodium hydroxide solution; practically all the ester was thus removed from the ether. After 20 minutes the alkaline solution was treated with an excess of dilute sulphuric acid. At first a yellow precipitate was formed but this redissolved when the mixture was shaken. The solution then became turbid, owing to the separation of drops of an oily liquid. After 14 hours the liquid had solidified and carbon dioxide was being evolved. When the acid solution was heated on a boiling water bath streams of carbon dioxide came off; this was completely soluble in 10 per cent sodium hydroxide. The hot solution was filtered and allowed to cool. It deposited about 4 grams of white crystals. These melted at 157° when dried on a clay plate and over concentrated sulphuric acid *in vacuo.* Analysis showed that the substance was phenylpyroracemic acid.[1]

0.1543 gram gave 0.3735 gram CO_2 and 0.0694 gram H_2O.

	Calculated for $C_9H_8O_3$.	Found.
C	65.85	66.01
H	4.88	4.99

The study of phenylmalonic nitrile and its derivatives is being continued.

UNIVERSITY OF CHICAGO,
Aug. 27, 1907.

Contributions from the Chemical Laboratory of Harvard College.

ON TRIBROMMETHOXYORTHOBENZOQUINONEMONOMETHYLHEMIACETAL.

BY C. LORING JACKSON AND H. A. FLINT.

In continuing the work[2] on derivatives of tetrabromorthobenzoquinone, which has been carried on for some time in this laboratory, we have made good progress in the study of the oxidation product, $C_5Br_4O_2$, discovered by Russe and one of us,[3] but we have decided to postpone the publication of our results until its constitution is entirely settled, which we hope to accomplish early in the following year.

In the present paper, we describe the tribrommethoxyorthoquinonemonomethylhemiacetal, the work on which is finished. Perhaps the most striking difference between the behavior of tetrachlor- and tetrabromorthoquinone with methyl and other alcohols lay in the fact that with the chlorine compounds

[1] *Cf.* W. Wislicenus: Ber. d. chem. Ges., **20**, 592. Erlenmeyer, jun.: Ann. Chem. (Liebig), **271**, 174.

[2] Jackson and Porter: THIS JOURNAL, **30**, 518 (1903); **31**, 89 (1904). Jackson and Carlton; **34**, 422 (1905). Jackson and Shaffer, **34**, 460 (1905). Jackson and Russe: **35**, 154 (1905). Jackson and MacLaurin: **37**, 87 (1907).

[3] *Ibid.*, **35**, 183 (1905).

the halogen is easily replaced, whereas, according to all previous work, the reaction with the bromine compound is confined to the quinone oxygen atoms. Thus tetrachlororthoquinone gave the following products:[1] $C_6Cl_3OCH_3O(OCH_3OH)$, $C_6Cl_3OHO_2$, $C_6Cl_2(OH)_2O_2$, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, and $C_6Cl_4OCH_3O_3HOC_6Cl_4$, the chlorine remaining unaffected only in the last. Tetrabromorthoquinone, under the same conditions, gave[2] $(C_6Br_4O_2)_4CH_3OH$ and $C_6Br_4OOCH_3OHOOC_6Br_4$, in neither of which is the halogen attacked. We have discovered now that, in making the α-compound (that last mentioned above) by the action of cold methyl alcohol on tetrabromorthoquinone, there is always formed, at the same time, a little of the tribrommethoxyorthoquinonemonomethylhemiacetal, $C_6Br_3OCH_3O(OCH_3OH)$, exactly analogous to the first body in the chlorine series,[3] which was overlooked before because it remained in solution in the methyl alcohol mother liquors. Its formation accounts for the small amount of hydrobromic acid so frequently observed during the preparation of the α compound. If the tetrabromorthoquinone is treated with hot, instead of cold, methyl alcohol, the tribromhemiacetal becomes the principal product, little, if any, of the α compound being formed. The previous statement that the halogen is not affected when the tetrabromorthoquinone is treated with methyl alcohol, therefore, is not true but must be changed to the following: tetrabromorthoquinone shows much less tendency than the tetrachlor compound to undergo attack on the halogen when treated with methyl alcohol, the reaction which affects the halogen remaining comparatively insignificant if the methyl alcohol acts in the cold, whereas with the tetrachlororthoquinone this is a principal reaction under these conditions.

The tribrommethoxyorthoquinonehemiacetal, $C_6Br_3OCH_3O(OCH_3OH)$, melts at 138°. This is strange, as the corresponding trichlor compound melts at 138°–140°. Its constitution was determined by convertin git into the acetyl compound, $C_6Br_3OCH_3O(OCH_3OC_2H_3O)$, which melts at 158° (the trichlor compound melts at 149°–150°). This proves that it contains one hydroxyl group. On treatment with phenylhydrazine, the acet compound was converted into the phenylhydrazone, $C_6Br_3OCH_3N_2HC_6H_5(OCH_3OC_2H_3O)$, melting at 205° (whereas the trichlor hydrazone melts at 235°), which proves the presence of the carbonyl group of the quinone. These two observations establish the fact that it is a monohemiacetal.

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[1] THIS JOURNAL, **38**, 127 (1907).

[2] *Ibid.*, **31**, 95 (1904); **34**, 425 (1905).

[3] *Ibid.*, **38**, 142 (1907).

When heated with hydrobromic acid, it is converted into the oxyquinone, $C_6Br_3OHO_2$, red plates melting at 205°, which so closely resembles, in all its properties, the trichloroxyparaquinone melting at 198° that we feel convinced it is also a paraquinone, the purple solution formed from each compound with water or alcohol being particularly distinctive. On the other hand, the tribrom compound is decidedly redder than the chlorine body, but, as far as we can find, this deeper color might be produced by the presence of bromine, instead of chlorine, in the molecule, and, in any case, this difference is not sufficiently significant, in view of the many resemblances between the two bodies, to make it worth while to submit the constitution of this bromine compound to an experimental test.

If hydrochloric acid is used, instead of hydrobromic acid, for decomposing the hemiacetal, the product is a mixture of trichloroxyparaquinone with the tribrom compound in the proportion of about one part of the latter to three of the former. This replacement of bromine by chlorine under the influence of hydrochloric acid by warming on the steam bath in an open vessel is certainly striking. It should be remembered in this connection that, in the presence of a quinone, hydrochloric acid may be converted into free chlorine, but we do not think it probable that such a reaction takes place to any extent in this case, for the product is the oxyparaquinone and not the oxyhydroquinone as it would be if chlorine had been formed in quantity. We are inclined, therefore, to ascribe this replacement to the direct action of the hydrochloric acid.

Porter and one of us[1] thought a similar replacement of bromine by chlorine took place when the α-benzyl alcohol body,

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[1] THIS JOURNAL, **31**, 112 (1904).

$C_6Br_4OOC_7H_7OHOOC_6Br_4$, was heated with hydrochloric acid, but, in this case, the product was a pyrocatechin, not an orthoquinone. The α-water body, under the same conditions, gave a considerable amount of bromine. The study of this curious replacement of bromine by chlorine will be continued in this laboratory.

EXPERIMENTAL.

Preparation of Tetrabromorthobenzoquinone.—The tetrabrompyrocatechin was prepared by the action of bromine on pyrocatechin dissolved in glacial acetic acid as described in previous papers[1] of this series, but its conversion into the orthoquinone was carried on by the following method, which is less expensive and gives better yields than the oxidation in glacial acetic acid solution formerly used in this laboratory. Thirty grams of tetrabrompyrocatechin were dissolved in 30–35 cc. of ethyl alcohol and the solution cooled with ice water; 8 cc. of fuming nitric acid, diluted with 50–60 cc. of glacial acetic acid, were added, and the mixture stirred vigorously. It was then allowed to stand 10 minutes when about two-thirds of the tetrabromorthoquinone had separated from the solution. This was filtered out, washed thoroughly with water, and dried on a porous plate. The filtrate from the crystals was diluted with 500 cc. of water, which precipitated the dissolved tetrabromorthoquinone, and this was filtered quickly, washed thoroughly with water, and dried as before on a porous plate. The yield varied from 26–27 grams, so that, at best, it was nearly 90.5 per cent of the theoretical, whereas with the older method 24 grams, that is, 80.4 per cent of the theoretical, were obtained. The melting point of our quinone varied from 146° to 150°, apparently according to the purity of the tetrabrompyrocatechin. The older process gave melting points from 145° to 150°, the true melting point being 150°–151°; our product, therefore, was pure enough for our purposes.

Tribrommethoxyorthoquinonemethylhemiacetal, $C_6Br_3OCH_3O(OCH_3OH)$. — This substance was formed as a secondary product in the preparation of the α compound, $(C_6Br_4O_2)_2CH_3OH$, by the action of cold methyl alcohol on tetrabromorthoquinone. Its formation accounts for the small amount of hydrobromic acid always observed in making the α compound. It remained dissolved in the methyl alcohol after the α compound had crystallized out, and was obtained by evaporating these mother liquors either by heat or spontaneously, after which the yellow residue was crystallized from a mixture of equal parts of benzene and ligroin until it showed the constant melting point 138°.

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[1] This Journal, **26**, 34 (1901); **34**, 460 (1905).

The substance can be obtained as the principal product as follows: one part of tetrabromorthoquinone was boiled with 10–12 parts of methyl alcohol on the steam bath in a flask with a return condenser for one and a half to two hours. At the end of this time the solution had taken on a much lighter color, and then about 8 parts of the methyl alcohol were distilled off and the remainder allowed to evaporate. The residue was purified as before by crystallization from equal parts of benzene and ligroin, until it showed the constant melting point 138°, when it was dried *in vacuo* for analysis.

I. 0.3632 gram substance gave 0.3140 gram CO_2 and 0.0584 gram H_2O.

II. 0.3608 gram substance gave 0.3151 gram CO_2 and 0.0572 gram H_2O.

III. 0.1021 gram substance gave 0.1411 gram AgBr.

IV. 0.1383 gram substance gave 0.1910 gram AgBr.

	Calculated for $C_6Br_3OCH_3O(OCH_3OH)$.	Found.			
		I.	II.	III.	IV.
C	23.59	23.58	23.82	. .	.
H	1.72	1.80	1.77	. .	. .
Br	58.96	. .	. .	58.81	58.77

Properties of Tribrommethoxyorthoquinonemonomethylhemiacetal.—It crystallizes in yellow plates which melt at 138° to a colorless liquid. It is easily soluble in ethyl or methyl alcohol, ether, chloroform, benzene, toluene, or glacial acetic acid; slightly soluble in ligroin or in hot water, which gives a purple solution. Strong hydrochloric acid converts it into an orange product which will be described later; strong sulphuric acid dissolves it with a red color; strong nitric acid acts in the same way but more slowly; aqueous sodic hydrate acts on it at once, giving a dark orange color.

Tribrommethoxyorthoquinonemonomethylacetacetal, $C_6Br_3OCH_3O(OCH_3OC_2H_3O)$.—Three grams of the hemiacetal were heated with 15 cc. of acetic anhydride on the steam bath in a flask with a return condenser for half an hour. On cooling, nearly white crystals were deposited which were purified by crystallization from a mixture of equal parts of benzene and ligroin until they showed the constant melting point 158°, when they were dried *in vacuo* for analysis.

0.1678 gram of substance gave 0.2112 gram AgBr.

	Calculated for $C_6Br_3OCH_3O(OCH_3OC_2H_3O)$.	Found.
Br	53.45	53.56

Properties of Tribrommethoxyorthoquinonemonomethylacetacetal.—It crystallizes from a mixture of benzene and ligroin in slightly yellow crystals, apparently of the orthorhombic system, which melt at 158° to a colorless liquid. It is freely soluble in ether, acetone, benzene, or toluene; slightly soluble in ethyl alcohol, more so in methyl alcohol; practically insoluble in ligroin or water. Strong hydrochloric acid or strong nitric acid has no effect on it; strong sulphuric acid gives with it a red solution; sodic hydrate in aqueous solution decomposes it, forming an orange solution.

Tribrommethoxyorthoquinonemonomethylacetacetalhydrazone, $C_6Br_3OCH_3N_2HC_6H_5(OCH_3OC_2H_3O)$.—One gram of the methylacetacetal just described was mixed with 10 cc. of phenylhydrazine and the mixture, after being warmed on the steam bath for a few minutes, was allowed to stand overnight. The white, crystalline product thus obtained was washed very thoroughly with benzene and ligroin, ligroin, alcohol, and ether, and then dried *in vacuo* for analysis. This method of purification was adopted because the product seems to be decomposed when it is dissolved, the crystals formed having a reddish color.

0.0872 gram of substance gave 0.0901 gram AgBr.

	Calculated for $C_6Br_3OCH_3N_2HC_6H_5(OCH_3OC_2H_3O)$.	Found.
Br	44.52	43.97

Properties of the Tribrommethoxyorthoquinonemonomethylacetacetalhydrazone.—It crystallizes in nearly white needles which melt at 205° to a red liquid. It is very slightly soluble in the common solvents, when cold, and, if heated with them, it is decomposed; thus, the solution in alcohol or benzene deposits reddish crystals. The three strong acids or sodic hydrate decompose it.

Tribromoxyparabenzoquinone, $C_6Br_3OHO_2$.—One gram of the tribrommethoxyorthoquinonehemiacetal was dissolved in a concentrated aqueous solution of hydrobromic acid and warmed on the steam bath for one hour. On cooling, red plates of the oxyparaquinone were deposited, which were purified by crystallization from a mixture of equal parts of benzene and ligroin until they showed the constant melting point 205°, when they were dried *in vacuo* for analysis.

0.1141 gram of substance gave 0.1784 gram AgBr.

	Calculated for $C_6Br_3OHO_2$.	Found.
Br	66.48	66.54

Properties of the Tribromoxyparaquinone.—It crystallizes in red plates which turn purple on exposure to the air and melt at 205°. It is freely soluble in ethyl or methyl alcohol; or ether, forming a purple solution; freely soluble in acetone, chloroform, benzene, or toluene with a reddish yellow color; slightly soluble in ligroin; soluble in water, forming a purple solution. Strong hydrochloric acid or hydrobromic acid dissolves it, apparently without alteration; strong nitric acid or sulphuric acid has no effect on it in the cold but decomposes it when hot; sodic hydrate dissolves it, forming a green solution, probably of the salt of the oxyquinone, which, on warming, turns purple from the formation of the chloranilate.

Action of Hydrochloric Acid on Tribrommethoxyorthoquinonehemiacetal.—If a few grams of the hemiacetal were dissolved in strong hydrochloric acid and the solution heated on the steam bath for half an hour, beautiful orange plates were deposited on cooling, which, after crystallization from a mixture of equal parts of benzene and ligroin, showed the constant melting point 195°. On submitting this substance to an analysis according to Carius, the argentic halide obtained was pure white and dissolved in ammonic hydrate with the utmost ease, showing that it was in great part argentic chloride. It seemed, therefore, that part, at least, of the tribrom compound had been converted into the corresponding trichlor compound by the action of hydrochloric acid. That this change was not complete was shown by the melting point, 195°, instead of 198° for the pure $C_6Cl_3OHO_2$, and by the analyses, which came about 1.5 per cent lower than the value calculated for pure AgCl. This view was confirmed by the detection of a little bromine in the argentic halide. According to our calculations, it is a mixture of about 3 parts of the chlor compound with one of the brom compound, as shown by the following analysis, which was confirmed by two others.

0.1362 gram of substance gave 0.2500 gram of mixed halides.

	Calculated for $3C_6Cl_3OHO_2.C_6Br_3OHO_2$.	Found.
3Cl + Br	53.58	53.54

As was to be expected, the mixture resembled its two components in the strongest way in its properties; as did also the acet body formed from it, which melted at 113° instead of 127°, the melting point of the pure trichlor compound and, on analysis, also gave results indicating the presence of the two halogens.

We are at present continuing the study of the derivatives of tetrabromorthoquinone in several other directions.

Cambridge, Mass.,
August 4, 1907.

METHYLDINORMALPROPYLMETHANE.

By Latham Clarke.

A research on the hydrocarbons of the formula C_8H_{18} is now in progress in this laboratory. In the course of this investigation, all the possible isomers will be prepared and a study made of their chemical and physical properties. At the present time, five of the eighteen possible octanes have been synthesized, *viz.*, normal octane,[1] diisobutyl,[2] 3-methylheptane,[3] dimethyl-3-

[1] Riche: Ann. Chem. (Liebig), **117**, 265. Schorlemmer: *Ibid.*, **161**, 280; **147**, 227; **152**, 152. Zincke: *Ibid.*, **152**, 15. Paterno and Peratoner: Ber. d. chem. Ges., **22**, 467.

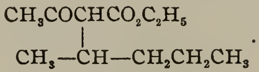
[2] Wurtz: Ann. Chem. (Liebig), **96**, 365. Schorlemmer: *Ibid.*, **114**, 188. Koch: *Ibid.*, **69**, 261.

[3] Welt: Ann. Chim. Phys., [7]. **6**, 121.

4-hexane,[1] and hexamethylethane.[2] Of the remaining thirteen, the first to be synthesized was 2-methylheptane, or methyldinormalpropylmethane, described in this paper.

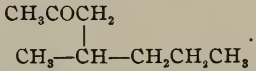
The method which seemed best adapted for obtaining this octane in a state of highest purity was that given in the following series of reactions:

Methylnormalpropyl ketone was prepared from ethyl acetate by saponification; on reduction, this yielded methylnormalpropylcarbinol, which, in turn, was transformed into the corresponding carbinol iodide. The sodium salt of acetacetic ester was then treated with this iodide, giving ethyl β-amylacetacetate,



$$\begin{array}{c}\mathrm{CH_3COCHCO_2C_2H_5}\\ |\\ \mathrm{CH_3-CH-CH_2CH_2CH_3}\end{array}.$$

By saponification of this, β-amylacetone was obtained,

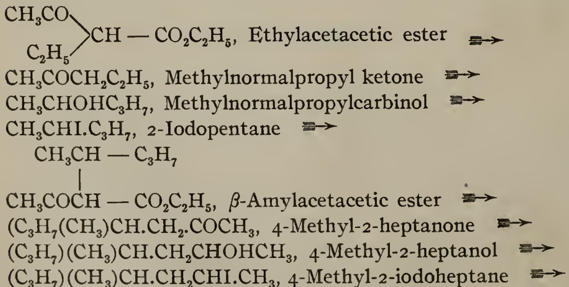


$$\begin{array}{c}\mathrm{CH_3COCH_2}\\ |\\ \mathrm{CH_3-CH-CH_2CH_2CH_3}\end{array}.$$

This was transformed into the corresponding carbinol and then into carbinol iodide which, by reduction, gave an octane having the structure

$$\mathrm{CH_3CH_2CH_2.CH(CH_3)CH_2CH_2.CH_3}.$$

The whole series of reactions is concisely expressed in the following summary:



$\left.\begin{array}{l}\mathrm{CH_3CO}\\ \mathrm{C_2H_5}\end{array}\right>\mathrm{CH-CO_2C_2H_5}$, Ethylacetacetic ester $\rightarrow$

$\mathrm{CH_3COCH_2C_2H_5}$, Methylnormalpropyl ketone $\rightarrow$

$\mathrm{CH_3CHOHC_3H_7}$, Methylnormalpropylcarbinol $\rightarrow$

$\mathrm{CH_3CHI.C_3H_7}$, 2-Iodopentane $\rightarrow$

$\begin{array}{l}\mathrm{CH_3CH-C_3H_7}\\ \quad|\\ \mathrm{CH_3COCH-CO_2C_2H_5}\end{array}$, β-Amylacetacetic ester $\rightarrow$

$\mathrm{(C_3H_7(CH_3)CH.CH_2.COCH_3}$, 4-Methyl-2-heptanone $\rightarrow$

$\mathrm{(C_3H_7)(CH_3)CH.CH_2CHOHCH_3}$, 4-Methyl-2-heptanol $\rightarrow$

$\mathrm{(C_3H_7)(CH_3)CH.CH_2CHI.CH_3}$, 4-Methyl-2-iodoheptane $\rightarrow$

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[1] Norris and Green: This Journal, **26**, 313 (1901).

[2] Henry: Compt. rend., **142**, 1075 (1906).

$(C_3H_7)(CH_3)CH.CH_2CH_2CH_3$, 4-Methylheptane or Methyldinormalpropylmethane.

EXPERIMENTAL.

Methylnormalpropyl Ketone.

Ethyl ethylacetacetate was made from ethyl acetacetate by Conrad's method.[1] It was found that in this reaction from 2 to 10 per cent of the diethyl derivative was always produced, but it was more convenient to postpone the separation of the two products until the corresponding ketones were obtained, when, by fractional distillation, the two derivatives were completely separated.

The impure ethyl ethylacetacetate was boiled for ten hours with 10 per cent caustic potash solution, using three molecules of potassic hydrate to one of the acetate. The mixture was then distilled with steam, the upper layer of the distillate separated, washed once with water, dried over calcic chloride, and fractionated with a long Hempel column. After five distillations, two portions were obtained, one boiling at 101.8° and the other at 138°; the first was methylnormalpropyl ketone, the second, 3-ethyl-2-pentanone. From 200 grams of the mixed ethyl acetacetate and diethyl acetacetate, 75 grams of the first ketone and 6 to 7 grams of the second were usually obtained.

Methylnormalpropylcarbinol.

This carbinol has been prepared by Friedel[2] and also by Belohoubek[3] by reduction of methylnormalpropyl ketone with sodium amalgam, but the reduction can be carried out much more satisfactorily by the method described in the following experiment:

190 grams of methylnormalpropyl ketone were dissolved in 360 grams of ether and the solution poured over 320 grams of water in a large flask provided with a long return condenser. 105 grams of sodium were added piece by piece, in the course of two or three hours, and when the reaction ceased, the ethereal layer was separated and fractionated. After three distillations, there were obtained 102 grams of a portion boiling at 119° under 760 mm. pressure and consisting of methylnormalpropyl-

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[1] Conrad and Limpach: Ann. Chem. (Liebig), **192**, 153.

[2] Jahres. d. Chem., **1869**, 513.

[3] Ber. d. chem. Ges., **9**, 924.

carbinol, and 35 grams of a portion boiling at 220°–224° and consisting of symmetrical dimethyldipropylglycol. The yield of the carbinol was about 52.5 per cent of the theoretical.

2-Iodopentane.

Methylnormalpropylcarbinol was transformed into 2-iodopentane by allowing a mixture of 56 grams of carbinol, 70 grams of iodine, and 7 grams of red phosphorus to stand at room temperature for one hour, and then heating it on the water bath for three hours. The mixture was distilled, the iodide separated, washed with water and very dilute caustic potash solution, and dried over calcic chloride. The iodide was not redistilled. The yield in this experiment was about 104 grams.

Preparation of Ethyl β-Amylacetacetate.

It was found by experiment that Conrad's[1] method for the preparation of acetacetic ester derivatives worked very poorly with 2-iodopentane and ethyl acetacetate, the reaction yielding almost none of the expected product, but giving instead ethyl-β-amylether, propylethylene, and several other by-products. Accordingly, the following procedure was employed in the synthesis of ethyl β-amylacetacetate.

85 grams of ethyl acetacetate were dissolved in 200 grams of pure benzene, and 15 grams of sodium were added. Toward the end the sodium dissolved very slowly, although the reaction was carried out on the steam bath, and the few small pieces of sodium remaining undissolved after an hour were removed with a platinum spatula. To the solution were added 97.5 grams of 2-iodopentane, which is three-fourths the theoretical quantity demanded by the given weight of ethyl acetacetate, but these quantities were used because the 2-iodopentane was more valuable than the ethyl acetacetate and it was desirable, therefore, to get the best possible result from the former at the expense of some of the latter. The amount of sodium removed was so small (usually less than half a gram) that the sodium ethyl acetacetate was always present in excess.

The benzene solution of sodium ethyl acetacetate and 2-iodopentane was heated on the water bath with a reflux condenser for 15 hours, and then set aside for 5–6 hours. During this time the sodium iodide separated out and formed a layer on the bottom of the flask. The clear solution was decanted and then was heated on a calcic chloride bath (boiling point 120°) and about three-fourths of the benzol distilled off. The first runnings consisted of about one gram of a liquid boiling at 39°, which later was found to be propylethylene. This undoubtedly was formed from 2-iodopentane by the splitting off of hydriodic acid in the alkaline solution. Analysis gave the following result:

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[1] *Loc. cit.*

0.2995 gram substance gave 0.8570 gram CO_2 and 0.3861 gram H_2O.

	Calculated for C_5H_{10}.	Found.
C	85.71	85.84
H	14.28	14.32

Towards the end of the distillation considerable sodium iodide separated out and the solution was shaken vigorously to prevent bumping. The residue was treated with twice its volume of water. After standing a few minutes a copious crop of needles was deposited. Some separated out in the water, but in the benzol-ester mixture the needles were so thickly deposited that it became jellylike and could be almost inverted without spilling. The water was drawn off and filtered and the needles recrystallized from alcohol twice. The melting point was then constant at 169°.

The benzene solution was filtered and the needles were recrystallized twice from alcohol. The melting point, 169°, showed that they were identical with those obtained from the water. The yield of these crystals was four grams, thus showing that this body was only a small by-product.

Study of the White Needles.

Analysis gave the following results:

I. 0.1133 gram substance gave 0.2637 gram CO_2 and 0.0742 gram H_2O.

II. 0.1343 gram substance gave 0.3151 gram CO_2 and 0.0868 gram H_2O.

III. 0.1305 gram substance gave 0.3031 gram CO_2 and 0.0876 gram H_2O.

	Calculated for $C_{11}H_{16}O_4$.	Found. I.	II.	III.
C	63.30	63.46	63.77	62.91
H	7.37	7.27	7.15	7.45

These analyses show that the formula for the substance is $C_{11}H_{16}O_4$ or some multiple of this.

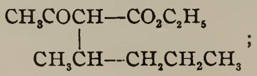
Properties.—This substance crystallizes from 95 per cent ethyl alcohol in long, fibrous, white needles; it is very soluble in hot alcohol but only moderately so in the cold. It is soluble also in acetone, acetic ester, benzol, and methyl alcohol; insoluble in water. It dissolves readily in aqueous caustic potash, giving a yellow solution which soon turns red. The yellow solution, when treated with dilute hydrochloric acid, precipitates the white substance unchanged, but when hydrochloric acid is added to the red solution after the latter has been boiled a few minutes, a red substance is thrown down which is entirely different from the original white body.

It is hoped that this interesting compound can be further studied within the next few months.

Ethyl β-Amylacetacetate.

The filtrate from the white crystals, after being dried over dehydrated potassic carbonate, was fractionated and yielded 56 grams of a liquid, boiling at 226° under 760 mm. pressure, which, as is shown later, was ethyl β-amylacetacetate. The yield was about 57 per cent of the theoretical amount as calculated from the weight of 2-iodopentane used.

The method of formation from 2-iodopentane and sodium ethyl acetacetate proves that the formula for β-amylacetacetate is



$$\begin{array}{l} CH_3COCH{-}CO_2C_2H_5 \\ \qquad\quad | \\ \qquad CH_3CH{-}CH_2CH_2CH_3 \end{array} ;$$

This was further shown by analysis.

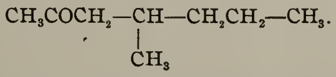
0.2074 gram substance gave 0.5063 gram CO_2 and 0.1781 gram H_2O.

	Calculated for $C_{11}H_{20}O_3$.	Found.
C	66.00	66.58
H	10.00	9.55

Properties.—This compound is an oily liquid boiling at 226° under 760 mm. pressure, has a pleasant characteristic odor like that of dandelions, and mixes with ether, ethyl alcohol, methyl alcohol, toluene, benzene, chloroform, and glacial acetic acid.

β-Amylacetone or 4-Methyl-2-heptanone.

Ethyl β-amylacetacetate was boiled for ten hours with three molecules of caustic potash, in ten per cent solution, in a large flask fitted with a reflux condenser; the resulting liquid was distilled with steam and the upper layer of the distillate separated, dried over calcic chloride, and distilled with a Hempel column. After three fractionations of the portion boiling at 150°–165°, practically all the liquid collected in one fraction boiling at 156° under 760 mm. of pressure. A small amount of unchanged ethyl β-amylacetate was usually found to be present after the treatment with alkali, but this was removed by the subsequent distillation. The fraction boiling at 156° was β-amylacetone or 4-methyl-2-heptanone,



$$\mathrm{CH_3COCH_2{-}\underset{\substack{|\\ CH_3}}{CH}{-}CH_2CH_2{-}CH_3.}$$

The usual yield was fifty per cent of the theoretical, 50 grams of ethyl β-amylacetacetate giving about 17 grams of the ketone.

Experiments with sulphuric acid as the hydrolyzing agent gave much poorer yields.

Analysis gave the following results:

0.1531 gram substance gave 0.4198 gram CO_2 and 0.1742 gram H_2O.

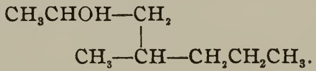
	Calculated for $C_8H_{16}O$.	Found.
C	75.00	74.78
H	12.50	12.64

Properties.—β-amylacetone boils at 156°, has a strong, pleasant, and very characteristic odor like that of bananas, and is soluble in ether, ethyl alcohol, methyl alcohol, benzene, toluene, chloroform, and glacial acetic acid.

4-Methyl-2-heptanol.

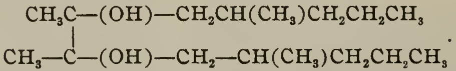
This compound was formed from β-amyl ketone by reduction in the following manner:

Four parts of ketone, by weight, were dissolved in eight parts of ether and poured over seven parts of water. Sodium, two parts, was added slowly in small pieces, and when the metal had completely dissolved the ethereal layer was separated and distilled. The ethereal residue, on fractionating, collected in two parts, one boiling at 160°–175° and the other, of which there was only a small quantity, boiling much higher, roughly between 285°–290°. The first fraction was redistilled three times and yielded a liquid boiling quite sharply at 168° under 762 mm. pressure. This was the carbinol,



$$\begin{array}{l} \mathrm{CH_3CHOH{-}CH_2} \\ \qquad\qquad\quad\;\; | \\ \qquad\quad \mathrm{CH_3{-}CH{-}CH_2CH_2CH_3}. \end{array}$$

The second fraction was not studied further, as the quantity at hand was small, but it was without doubt a pinacone having the formula



$$\begin{array}{l} \quad\;\; \mathrm{CH_3C{-}(OH){-}CH_2CH(CH_3)CH_2CH_2CH_3} \\ \qquad\quad\; | \\ \mathrm{CH_3{-}C{-}(OH){-}CH_2{-}CH(CH_3)CH_2CH_2CH_3}. \end{array}$$

In a typical experiment, 16 grams of ketone yielded 14 grams of carbinol and one gram of pinacone. It will be noticed that the proportion of pinacone formed in this reaction is much smaller than is usual in such reductions. It was found that when the reduction took place rapidly the amount of pinacone produced was smaller than when the reduction was slow. In some cases, less than half a gram of pinacone was formed; in other cases, five grams were produced.

Analysis of 4-methyl-2-heptanol gave the following results:

0.1498 gram substance gave 0.4055 gram CO_2 and 0.1871 gram H_2O.

	Calculated for $C_8H_{18}O$.	Found.
C	73.85	73.82
H	13.85	13.88

Properties.—It boils at 168° under 762 mm. pressure, has an odor like dilute commercial amyl alcohol, and is soluble in ether, ethyl alcohol, methyl alcohol, benzene, toluene, chloroform, and glacial acetic acid.

Preparation and Reduction of 2-Iodo-4-methylheptane.

The carbinol just described was heated to 100° on the water bath and hydriodic acid gas[1] passed in until the saturation point was reached. After standing an hour, more hydriodic acid gas was passed into the liquid, which now consisted mainly of 2-iodo-4-methylheptane. This was neither distilled nor even washed with water, but was dissolved in an equal volume of methyl alcohol and the flask containing it connected to a return condenser. A few cubic centimeters of concentrated hydrochloric acid (38 per cent) and several grams of granulated zinc were added to the solution. The evolution of hydrogen began at once. The flask warmed up and was kept at a temperature of about 45° by immersing it in a bath of warm water. From time to time, sufficient hydrochloric acid was added to keep up a vigorous action and care was taken to have the zinc present in large excess. After the action had continued for several minutes, a floating oily layer began to separate out. This increased slowly and in about 15 hours seemed to have reached a maximum. It was separated, dried over calcic chloride, and distilled. The first fraction of the distillate consisted of a small amount of methyl alcohol; the second part came over between 110° and 125°; the portion boiling above 125° seemed to consist of unchanged carbinol and iodide. The heating was therefore stopped, the residue saturated with hydriodic acid gas, put back into the reduction flask, and the process repeated.

The fraction boiling at 110°–125° consisted principally of octane. It was shaken with concentrated sulphuric acid, then allowed to stand over concentrated sulphuric acid for two weeks, washed with aqueous caustic soda, and treated with metallic sodium. The liquid was kept over sodium for a month and was finally boiled for several hours with a return condenser.

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[1] Prepared by the method described in Gatterman's "Pract. Meth. Org. Chem.," 2nd edition, p. 345.

This long treatment was found to be necessary to remove the last traces of halogen, which are held with great tenacity. The liquid, on distillation, boiled sharply at 118° under 760 mm. pressure and was found to be the octane methyldinormalpropylmethane, or 4-methylheptane. The yield was usually about 40 per cent of the theoretical.

Methyldinormalpropylmethane.

The hydrocarbon obtained by the reduction described above is a colorless, mobile liquid, almost odorless, and entirely free from halogen. Its constitution is proven beyond question by the method of its formation.

Analysis: 0.1449 gram substance gave 0.4466 gram CO_2 and 0.2097 gram H_2O.

	Calculated for C_8H_{18}.	Found.
C	84.21	84.05
H	15.79	16.08

Properties.—This octane boils sharply at 118° under 760 mm. pressure. At 15° its specific gravity is 0.7217. Its index of refraction, as determined by Mr. A. C. Boylston, who used a Pulfrich refractometer, is n D (25°) = 1.3978.

I am deeply indebted to the C. M. Warren fund for materials used in this research.

CAMBRIDGE, MASS.,
May 6, 1907.

ON THE DETECTION OF OZONE, NITROGEN PEROXIDE, AND HYDROGEN PEROXIDE IN GAS MIXTURES.

BY EDWARD H. KEISER AND LEROY MCMASTER.

When air is acted upon in a number of ways, such as by electric sparks, the flaming arc, burning hydrogen, burning magnesium, heated platinum wire, etc., in short, by any means which produce very high temperatures, ozone, nitrogen peroxide, and hydrogen peroxide may be formed. The silent electric discharge and the slow oxidation of phosphorus produce oxidizing gases in air. Several commercial processes of treating air so as to convert it into a more active chemical agent are at present in use. It is desirable, therefore, to have characteristic reactions for each of the three substances above mentioned in examining the gases produced in these different ways.

A great many reagents have been suggested for this purpose but many of these have been found to be unreliable, while others are not very sensitive, and still others are rare substances that are not easily obtained. The following table contains a list of such substances, together with a statement of their behavior toward ozone, nitrogen peroxide, and hydrogen peroxide.

	Ozone.	Nitrogen peroxide.	Hydrogen peroxide.
Potassium iodide and starch[1]	blue	blue	blue
Wine-red litmus paper moistened with potassium iodide[2]	blue	no change	blue
Tetramethylparaphenylenediamine[3]	bluish violet	bluish violet	bluish violet
Metaphenylenediamine, alkaline solution[4]	Burgundy red or yellow	no change	no change
Manganese chloride paper moistened with guiacum tincture[5]	blue	blue	no change
Benzidine in alcohol[6]	brown	blue	no change
Tetramethyl-*p*-*p*-diaminodiphenylmethane in saturated alcoholic solution[7]	violet	yellow	no change
Potassium ferricyanide and ferric chloride[8]	no change	no change	blue

[1] Schoenbein: Ber. u. d. Verh. d. Nat. Ges., Basel, **4**, 58.

[2] Houzeau: Ann. Chim. Phys., [4], **5**, 20.

[3] Wurster: Ber. d. chem. Ges., **19**, 3195.

[4] Erlwein and Weil: *Ibid.*, **31**, 3158.

[5] Engler and Wild: *Ibid.*, **29**, 1940.

[6] Arnold and Mentzel: *Ibid.*, **35**, 1324.

[7] *Ibid.*

[8] Schoenbein, Weltzien, also Schoene: *Ibid.*, **7**, 1695. Engler and Wild: *Ibid.*, **29**, 1940.

	Ozone.	Nitrogen peroxide.	Hydrogen peroxide.
Manganese dioxide or copper oxide[1]	decomposed	no change	decomposed
Silver foil[2]	black	no change	no change
Chromic acid and ether[3]	no change	no change	blue
Chromic acid[4]	no change		decomposed
Titanium hydroxide in sulphuric acid[5]	no change	no change	yellow
Thallous salts[6]	brown	no change	no change
Ammonium molybdate in sulphuric acid[7]	no change	no change	yellow
Guiacum tincture with malt infusion[8]	no change	no change	blue
Gold chloride free from acid[9]	black	no change	
Nitrite test with sulphanilic acid and α-naphthylamine[10]	no change	pink	no change

Arnold and Mentzel[11] have studied a number of the reagents that are mentioned in the preceding list. They find that potassium iodide and starch, and zinc iodide and starch, as well as guiacum tincture, give a blue color with ozone, nitrogen peroxide, chlorine, and bromine. In short, these reagents are not characteristic of anything more than an oxidizing gas. Red litmus paper moistened with potassium iodide solution they find to be entirely unreliable, because all paper turns blue with free iodine, and any gas that liberates iodine will turn the paper blue. They also found that a solution of potassium iodide to which wine-red litmus solution had been added was unsatisfactory, because the ozone acts upon the litmus and changes it to a green color. The third reagent in the above list, tetramethylparaphenylenediamine, is also turned blue by all oxidizing gases. Metaphenylenediamine, the fourth one, was unsatisfactory because they found that nitrogen peroxide gave the same color as ozone, and all oxidizing gases give yellowish colors with this substance. Silver foil[1] is not satisfactory because it is not at all sensitive. Arnold and Mentzel recommend an alcoholic solution of benzidine or, still better, an alcoholic solution of tetramethyl-*p*-*p*-diaminodiphenylmethane. This gives a violet color with ozone and yellow with nitrogen peroxide; with hydrogen peroxide it remains unchanged. They found, however, that the ozone obtained by the action of sulphuric acid upon barium dioxide had a different action upon this reagent; instead of violet a green color was obtained. Benzidine, under the same conditions, gave a blue instead of a brown color. Similar effects were obtained with the ozone from persulphates, percarbonates, and from sodium and hydrogen peroxides.

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[1] Andrews and Tait: Ann. Chem. (Liebig), **112**, 135.

[2] Ber. d. chem. Ges., **35**, 1326.

[3] Barreswill: Ann. Chim. Phys., [3], **20**, 364.

[4] Engler and Wild: Ber. d. chem. Ges., **29**, 1940

[5] Schoenn: Z. anal. Chem., **9**, 41.

[6] Schoene: Ann. Chem. (Liebig), **196**, 58.

[7] Schoenn: Z. anal. Chem., **9**, 41.

[8] Struve: *Ibid.*, **8**, 274.

[9] Boettger: *Ibid.*, **19**, 105.

[10] Bull. Soc. Chim., [3], **2**, 347 (1889).

[11] Ber. d. chem. Ges., **35**, 1324.

F. Fischer and Marx[1] have used tetramethyl-*p*-*p*-diaminodiphenylmethane or "tetramethyl base," as it is called, in their investigations upon the formation of ozone and nitrogen peroxide in air at high temperatures. They prepared ozone by the silent electric discharge in the Siemen's ozonometer, by the action of ultraviolet light, by the electrolysis of sulphuric acid, and in other ways, and found that ozone produces with this reagent a violet color and the oxides of nitrogen a yellow color. Mixtures of both gases give a dirty brown color intermediate between violet and yellow. Another fact that they emphasize is that the paper must always be kept moist; if it becomes dry, ozone changes it to a yellow color. To detect very small quantities of nitrogen oxides in the presence of ozone they recommend that the gas be conducted into liquid air. The ozone will dissolve while the oxides of nitrogen will separate as blue flakes. When the liquid air is then filtered, the frozen oxides of nitrogen remain upon the filter. The filtrate is allowed to boil, the air distils away, and the ozone remains. In this way both can be separately identified.

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[1] Manchot and Kampschulte (Ber. d. chem. Ges., **40**, 2891) have recently shown that while silver foil is not at all sensitive at ordinary temperatures, it becomes much more so at 220°-240° C. For metallic mercury they found the temperature at which action was strongest to be 170° C.

[2] *Ibid.*, **39**, 2555.

This method is open to the objection that liquid air is not readily obtained in many places. Likewise, the "tetra base" of Wurster and the "tetramethyl base" of Arnold and Mentzel are not easily obtainable substances. Moreover, the color changes are not always satisfactory. Thallous salts and titanic acid are not always at hand. We have now, however, devised a method which is free from these objectionable features and enables us to identify each of these three substances in the presence of the others.

We found that potassium permanganate, even in very dilute solution, is not decolorized by ozone. Nitrogen peroxide and hydrogen peroxide, on the other hand, both reduce it instantly. To identify ozone in gases that contain at the same time nitrogen peroxide and hydrogen peroxide it is only necessary to draw the gases through a solution of potassium permanganate; the nitrogen peroxide and the hydrogen dioxide will not pass through, while the ozone will, and can then be detected with potassium iodide and starch.

To detect nitrogen peroxide in the presence of ozone and hydrogen peroxide we take advantage of the fact that both ozone and hydrogen peroxide are decomposed when passed through a tube containing powdered manganese dioxide. Nitrogen peroxide passes through unchanged. Its presence can be shown by passing the gas, after it has gone over the manganese dioxide, into very dilute permanganate. If the latter is decolorized, nitrogen peroxide was present. A still more delicate test for nitrogen peroxide is this: pass the gas, which may contain ozone and hydrogen dioxide, directly into pure caustic soda, made from metallic sodium and nitrite-free distilled water, and then test the caustic soda solution for nitrites by the well-known sulphanilic acid and α-naphthylamine method.

Hydrogen dioxide can be identified in the presence of both ozone and nitrogen peroxide by passing the gas mixture into a solution of potassium ferricyanide and ferric chloride. The yellow brown solution becomes green and then blue as more hydrogen dioxide passes in. This formation of Prussian blue is characteristic of hydrogen dioxide and is not produced by either ozone or nitrogen peroxide. This we have found by experiment.

I. Examination of the Gases Produced by Burning Hydrogen in Air.

We have tried our method in the examination of the gases produced by burning hydrogen in air. A jet of burning hydrogen was introduced into the end of a glass tube fifteen millimeters in diameter. A current of air was drawn into the tube by means of an aspirator. The gas passed from the tube through a moderately strong solution of potassium permanganate and then into a solution of potassium iodide and starch. This soon became blue, thus showing that ozone was formed by the hydrogen burning in a rapid current of air. The potassium permanganate wash bottle was then replaced by a tube forty centimeters in length, filled with powdered manganese dioxide. Between this tube and the aspirator, a wash bottle with a very weak solution of potassium permanganate was inserted. Air was now rapidly drawn through the apparatus and the products of combustion of the hydrogen passed first over the manganese dioxide and then into the dilute permanganate. The latter, after a time, became decolorized, thus showing that nitrogen peroxide was formed. This was confirmed by passing the gases formed by burning hydrogen into a solution of nitrite-free caustic soda and then applying the nitrite test (Griess test) after having slightly acidified the solution. The pink color was formed, thus confirming the result obtained with dilute permanganate. The gases formed by burning hydrogen were also tested for hydrogen peroxide by drawing them through a solution of potassium ferricyanide and ferric chloride. This became first green, then blue, thus showing that hydrogen peroxide was present. This ferricyanide and ferric chloride test for hydrogen peroxide we found to be more sensitive than titanium dioxide in sulphuric acid.

The latter failed to show the presence of hydrogen peroxide in the gases produced by burning hydrogen in air.

II. Examination of the Gases Produced by the Silent Electric Discharge in Air and Oxygen.

Atmospheric air was purified and dried by being drawn, by means of an aspirator, through a series of wash bottles containing silver sulphate, potassium permanganate, and pure concentrated sulphuric acid, and was then passed through a Siemens' ozonometer. The ozonometer was connected with the terminals of a Ruhmkorff coil which, in turn, was connected with a storage battery. The potential of the coil discharge terminals was 2160 volts. The air passing through the ozonometer in which the silent discharge was taking place was thereupon conducted through a very weak solution of potassium permanganate. No decolorization took place, although the ozonized air was passed for more than two hours. Ozone was shown to be present in quantity, not only by its action upon potassium iodide and starch after it had passed through the permanganate, but also by its odor and by the repeated perforation of the rubber tube that connected the last wash bottle with the aspirator. We were surprised to find that, under these conditions, no nitrogen peroxide was formed. A quantitative determination of the ozone showed that there was 0.00086 gram per liter. We also conducted the air directly from the ozonometer into pure caustic soda and tested this for nitrites by the Griess test but failed to obtain any. With potassium ferricyanide and ferric chloride the ozonized air failed to give a reaction for hydrogen peroxide. The same results, namely, the absence of nitrogen peroxide and hydrogen peroxide in air that had passed through the Siemens' ozonometer, were obtained when we omitted washing the air with silver sulphate, caustic soda, potassium permanganate, and sulphuric acid before it entered the ozonometer. These experiments show conclusively that it is possible to ozonize air without, at the same time, forming nitrogen peroxide and hydrogen peroxide. We have repeated the above experiments with oxygen, made from fused sodium peroxide and water, instead of air. We obtained no nitrogen peroxide nor hydrogen peroxide. A quantitative determination showed the presence of 0.0012 gram of ozone to the liter. This ozonized oxygen failed to decolorize potassium permanganate solution.

III. Examination of Gases Produced by the Action of Concentrated Sulphuric Acid upon Barium Dioxide.

Concentrated sulphuric acid was allowed to drop upon barium dioxide, contained in an Erlenmeyer flask, and the gases resulting were conducted through a concentrated solution of potassium permanganate in a Geissler potash bulb and then into a solution of potassium iodide and starch. A blue color soon appeared, thus showing the presence of ozone. The gas, after passing over manganese dioxide and then into permanganate, failed to give the reaction for nitrogen peroxide. Nor were we able to detect hydrogen peroxide by passing the gas through a solution of potassium ferricyanide and ferric chloride.

A small quantity of barium nitrate was now added to the barium dioxide and, on treating with concentrated sulphuric acid and testing as before, we obtained evidence of the presence of ozone and nitrogen peroxide, but not of hydrogen peroxide, in the gases given off.

IV. Examination of the Gases Produced by the Slow Oxidation of Phosphorus in Moist Air.

We have also used our method for the examination of the gases formed by the slow oxidation of phosphorus in air in the presence of water. We found ozone and nitrogen peroxide but no hydrogen peroxide.

V. Examination of the Gases Produced by the Action of the Flaming Electric Arc upon Air.

Air that had passed through the flaming electric arc of an Alsop process machine, such as is used in treating flour, was next examined by our method. We found that this air contained nitrogen peroxide, a trace of ozone, and a little hydrogen peroxide.

VI. Examination of Atmospheric Air.

We have applied our method to the examination of country air. Air from outside of the laboratory was drawn through a layer of absorbent cotton, six inches in length, then through a concentrated solution of potassium permanganate in a potash bulb, and finally into potassium iodide and starch. After the air had passed through for five hours, a faint blue color appeared, thus showing the presence of ozone. Air that was filtered through absorbent cotton and that had passed over a layer of manganese dioxide eighteen inches in length was conducted through a very faintly pink solution of permanganate. No decolorization was observed, although the air was drawn through for eighteen hours. We conclude from this that there was no nitrogen peroxide in the air. Air filtered through cotton was drawn through a solution of potassium ferricyanide and ferric chloride. After four hours the solution acquired a green color. We found, however, that the reagent used for detecting hydrogen dioxide, namely, a dilute solution of ferric chloride and potassium ferricyanide, when allowed to stand in air, gradually forms a green precipitate, even when protected from dust by being covered with a bell jar. We, therefore, drew atmospheric air for five hours through pure distilled water, contained in a potash bulb, and then tested this water with the reagent. We obtained no blue precipitate and, therefore, conclude that the green color mentioned above may not have been caused by hydrogen dioxide. These experiments prove that our method is sufficiently sensitive to show the presence of ozone in atmospheric air.

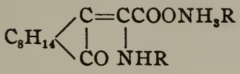
CHEMICAL LABORATORY,
WASHINGTON UNIVERSITY,
ST. LOUIS, April, 1907.

STUDY OF THE ACTION OF CERTAIN SECONDARY AMINES ON CAMPHOROXALIC ACID.

[ELEVENTH COMMUNICATION ON CAMPHOROXALIC ACID DERIVATIVES.[1]]

BY J. BISHOP TINGLE AND L. F. WILLIAMS.

In the course of an investigation by Bishop Tingle and Hoffman,[2] it was found that dimethylamine and diethylamine condense with camphoroxalic acid. The products consist, empirically, of 1 molecule of acid + 2 molecules of base, no water being eliminated. Compounds of secondary bases and ketones or enols had not, hitherto, been prepared. Consequently the bodies in question possessed a special interest and made us anxious to elucidate the subject more fully. We also wished to throw some light on the constitution of these substances. On comparing them with the condensation compounds of camphoroxalic acid and primary amines, it is seen that their constitution presents a decided peculiarity. Bishop Tingle and his coworkers have shown[3] that this acid condenses with primary amines, forming derivatives belonging to one of the three following types:



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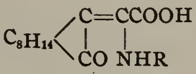
I.



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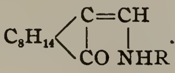
II.



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III.

From what has been said above, it will be apparent that the compounds from secondary amines resemble, in general, type I., but differ from it by containing, in addition, the elements of water. It has been shown in previous papers that in all probability substances of type I. are formed by the addition of the primary amine to the double linkage and also in some cases to the carboxyl group, giving the intermediate compound,

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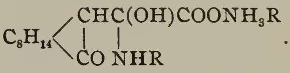
[1] The previous papers on this subject have appeared as follows: Inaug. Diss., (Munich), 1889, p. 34. J. Chem. Soc., **57**, 652 (1890). THIS JOURNAL, **19**, 393 (1897); **20**, 318 (1898); **21**, 238 (1899); **23**, 214 (1900). J. Am. Chem. Soc., **23**, 363 (1901). THIS JOURNAL, **34**, 217 (1905): **36**, 223 (1906). J. Am. Chem. Soc. 29 1242 (1907)

[2] THIS JOURNAL, **34**, 217 (1905).

[3] *Loc. cit.*

see errata
p. 882



$$C_8H_{14}\left\langle\begin{array}{l} CHC(OH)COONH_3R \\ \mid \qquad \mid \\ CO\ \ NHR \end{array}\right. .$$

As a rule, these intermediate bodies are unstable and readily eliminate water, passing into substances of type I.

Some of them, however, are quite stable. A number of these have been described in previous papers by the senior author and his coworkers,[1] and we ourselves have obtained two others, from ethylenediamine and paraminophenol, respectively, in the course of some work on primary amines and camphoroxalic acid. A paper on this investigation will be published in an early number of THIS JOURNAL. On account of the presence of the extra molecule of water in these substances, they have received the name of *camphoformolamine derivatives.*

With regard to the compounds of the secondary amines and camphoroxalic acid, it is not unnatural to suppose that they might be representatives of this intermediate, additive form. There are two reasons which, at present, lead us to reject this view of their constitution. The first and most important is based on the fact that they give an intense violet coloration with ferric chloride and alcohol. Compounds of types I. and II., from the primary amines, and also the addition products of these amines which have just been referred to, give no color with this reagent, whereas camphoroxalic acid itself gives a deep red color. It is well known that these pronounced colorations are characteristic of the group C:COH, consequently, although the derivatives of the secondary amines must, no doubt, differ from the parent acid, yet they must contain the group in question. A second consideration leading towards the same conclusion is this: Secondary aliphatic amines are, in general, more strongly basic than the corresponding primary compounds. Other things being equal, the readiness with which water is eliminated from a compound is decreased by the presence of negative groups in the molecule. Consequently, in so far as this reasoning is applicable to the case in question, the compound

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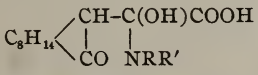
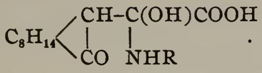
[1] *Loc. cit.*



should eliminate the elements of water *more* readily than a substance with the constitution



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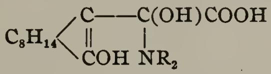
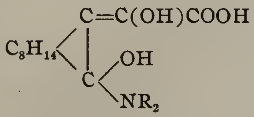
Actually, of course, the exact opposite is found to be the case. These considerations lead us, therefore, to the formula



as the best expression of the constitution of the compounds of camphoroxalic acid and the secondary amines. As in the case of almost all the derivatives of this acid which have been studied, it is based upon the assumption that the primary point of attack is the C:COH group. The grounds on which this belief is based have been fully discussed by Tingle and Robinson,[1] and need not be repeated here. Should subsequent work ever show them to be invalid, the only change which would be involved in the formulas given above would be the representation of the nitrogen atom as being linked to the ketonic instead of to the enolic carbon atom, thus



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The question at once arises as to the designation of these compounds. Until their constitution is definitely established, it appears to us that the simplest plan is to term them *iso-*

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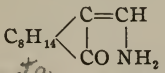
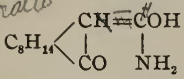
[1] This Journal, **36**, 223 (1906).

camphoformolamine derivatives; we have, then, three series of substances derived from the following complexes, *viz.*:



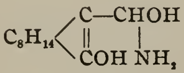
camphoformeneamine;

see errata p. 822



, *camphoformolamine*;

and

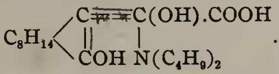


, *isocamphoformolamine.*

When these isocamphoformolaminecarboxylic acids, or their salts, are heated above their melting points, water and carbon dioxide are evolved, and products are obtained which are without action on ferric chloride and which resemble closely, in general properties, the compounds prepared, under corresponding conditions, from the condensation products of camphoroxalic acid and primary amines. They have, therefore, been formulated, in a manner similar to these latter, as alkyl or aryl derivatives of type III. given above. The secondary amines resemble the primary ones in that the ability of any individual one of them to form derivatives of both the isocamphoformolamine type or of type III. differs for each amine. This point is discussed more fully elsewhere in the present paper, *vide* p. 111.

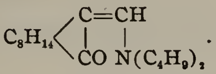
The first object of the investigation described in this paper was to apply the reaction discovered by Tingle and Hoffman to a number of other secondary amines. This has been done with a very considerable measure of success. The second object which we had in view was to obtain more experimental evidence for the formula which we have assigned to the compounds in question. This part of the work has been seriously interfered with by lack of the needed material which, though ordered early, did not reach us until too late to be of much use during the last academic year. The compounds named below have been studied. The nomenclature employed for the designation of the products of the reactions has been fully elucidated in the article by Tingle and Hoffman.[1]

1. *Diisobutylamine* and camphoroxalic acid give *diisobutylisocamphoformolaminecarboxylic acid*,

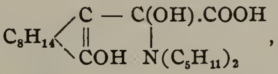


see errata p. 822

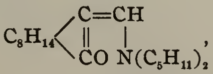
When this is heated above its melting point it forms *diisobutylcamphoformeneamine*,



2. *Diamylamine* gives *diamylisocamphoformolaminecarboxylic acid*,

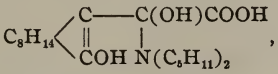


which forms *diamylcamphoformeneamine*,

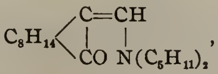


when heated above its melting point.

3. *Diisoamylamine* gives *diisoamylisocamphoformolaminecarboxylic acid*,



which is converted into *diisoamylcamphoformeneamine*,



when heated above its melting point.

4. *Dibenzylamine* and camphoroxalic acid react with greater

see errata p. 822.

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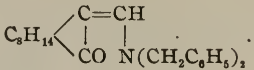
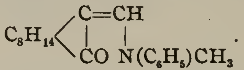
[1] *Loc cit.*

difficulty than the amines mentioned above. The product is *dibenzylcamphoformeneamine*,



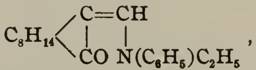
$$C_8H_{14}\left\langle\begin{matrix}C=CH\\ |\qquad|\\ CO\ \ N(CH_2C_6H_5)_2\end{matrix}\right. .$$

5. *Methylaniline* and camphoroxalic acid also react with some difficulty, forming *phenylmethylcamphoformeneamine*,



$$C_8H_{14}\left\langle\begin{matrix}C=CH\\ |\qquad|\\ CO\ \ N(C_6H_5)CH_3\end{matrix}\right. .$$

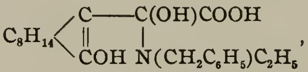
6. *Ethylaniline* gives *phenylethylcamphoformeneamine*,



$$C_8H_{14}\left\langle\begin{matrix}C=CH\\ |\qquad|\\ CO\ \ N(C_6H_5)C_2H_5\end{matrix}\right. ,$$

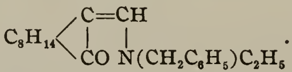
a viscous liquid.

7. *Benzylethylamine* gives *benzylethylisocamphoformolaminecarboxylic acid*,



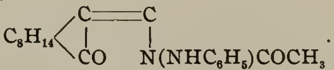
$$C_8H_{14}\left\langle\begin{matrix}C\text{——}C(OH)COOH\\ \|\qquad\quad|\\ COH\ \ N(CH_2C_6H_5)C_2H_5\end{matrix}\right. ,$$

which, when heated above its melting point, is changed to *benzylethylcamphoformeneamine*,



$$C_8H_{14}\left\langle\begin{matrix}C=CH\\ |\qquad|\\ CO\ \ N(CH_2C_6H_5)C_2H_5\end{matrix}\right. .$$

8. *Acetylphenylhydrazine* gives *acetylphenylaminecamphoformeneamine*,



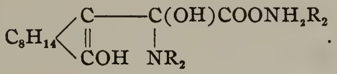
$$C_8H_{14}\left\langle\begin{matrix}C\text{===}C\\ |\qquad\qquad|\\ CO\quad N(NHC_6H_5)COCH_3\end{matrix}\right. .$$

The conduct of the following acyl secondary bases towards camphoroxalic acid was studied:

Paranitrobenzoylparaminophenol, diparanitrobenzoylparaminophenol, metanitrobenzoylparaminophenol, dimetanitrobenzoylparaminophenol, paranitrobenzoylorthoaminophenol, diparanitrobenzoylorthoaminophenol, metanitrobenzoylorthoaminophenol, dimetanitrobenzoylorthoaminophenol, phenylsulphoneparaminophenol, phenylsulphoneorthoaminophenol, diphenylsulphoneorthoamino-

phenol, and *paracetoaminophenol.* No single one of these acyl derivatives could, however, be induced to undergo reaction. Besides these we also investigated the behavior of *benzoylphenylhydrazine, benzylphenylhydrazine, benzylmethylamine, benzylaniline, phenylhydrazine-p-sulphonic acid, phenyl-β-naphthylamine*, and symmetrical *phenylmethylhydrazine.* These compounds also failed to react.

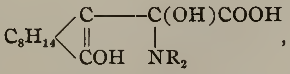
The preceding results permit of some rather interesting conclusions being drawn. In the case of the dimethyl- and diethylamine *two molecules* combine with *one* of camphoroxalic acid, forming a salt of the isoformolaminic acid,



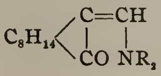
The remaining *aliphatic amines* which we have tried yield directly the *free acid* corresponding to the above salt. Tingle and Hoffman[1] were unable to prepare, from the salts of the dimethyl and diethyl compounds, the corresponding free acids. According to the system of nomenclature suggested by us, their two compounds should be termed *isocamphoformolamine*, not *camphoformolamine*, derivatives.

Evidently, therefore, the entrance of the more strongly basic, higher alkyl amine radical into the molecule of camphoroxalic acid has so weakened its acidic properties as to render it essentially a neutral body, incapable of salt formation. The gradation is a very interesting and delicate one.

In the case of the alkyl aniline derivatives which are, of course, feebler bases than the aliphatic amines, the acid type,



is rendered too unstable to be isolated, carbon dioxide and water are evolved spontaneously, and neutral products of the formula



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[1] *Loc. cit.*

are formed. The same is true of the condensation products of acetylphenylhydrazine and of dibenzylamine, which react like the alkyl anilines, whereas ethylbenzylamine reacts exactly like the aliphatic amines.

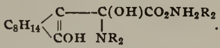
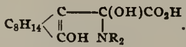
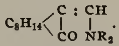
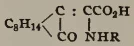
In the case of benzylaniline and of β-naphthylaniline, it is evident that the basic properties are too feeble to permit of condensation taking place under the most favorable conditions which we were able to employ. We do not think that our results lend any definite support to a theory of spatial hindrance, but it would be difficult to obtain a clearer or more delicate representation of the changes in the nature of the amines.

The condensation compound from acetylphenylhydrazine deserves a few words of separate treatment, not only because we believe that it is the *first* condensation product which has ever been obtained from this amine, but also because we think that it is the first acylated amine which has been induced to react with a ketonic or enolic compound. We have made a number of experiments to elucidate its constitution more fully. Although it apparently undergoes hydrolysis rather readily, it is difficult to purify the resulting compound unless the experimental conditions under which it is formed are regulated very carefully. The work in this connection will be continued by the senior author.

The failure to obtain a similar condensation compound from camphoroxalic acid and benzoylphenylhydrazine is, no doubt, to be ascribed to the more strongly negative nature of the benzoyl, as compared with the acetyl, group.

Of the remaining acylated amines (acylated aminophenols) which have been investigated, none of them showed any signs of a tendency to react with camphoroxalic acids.

At present it is unnecessary to discuss further these negative results, except to point out that the substances in question, if they exhibit basic properties at all, do so to an extremely slight degree. Their behavior confirms, therefore, the observations and conclusions made by ourselves and also by Bishop Tingle and his coworkers on the amine derivatives of camphoroxalic acid.

Secondary amines.	I.  $C_8H_{14}\left\langle\begin{array}{l}C\text{---}C(OH)CO_2NH_2R_2\\ \Vert\qquad\ \vert\\ COH\ \ NR_2\end{array}\right.$	II.  $C_8H_{14}\left\langle\begin{array}{l}C\text{---}C(OH)CO_2H\\ \Vert\qquad\ \vert\\ COH\ \ NR_2\end{array}\right.$	III.  $C_8H_{14}\left\langle\begin{array}{l}C : CH\\ \vert\quad\ \ \vert\\ CO\ \ NR_2\end{array}\right.$	IV.  $C_8H_{14}\left\langle\begin{array}{l}C : CCO_2H\\ \vert\quad\ \ \vert\\ CO\ \ NHR\end{array}\right.$
1. $NH(CH_3)_2$	137°·5*	....	163°*	
2. $NH(C_2H_5)_2$	139°·5*	....	153°*	
3. $NH(C_4H_9)_2$ *iso*	....	180°	73°–74°	
4. $NH(C_5H_{11})_2$	....	160°	43°	
5. $NH(C_5H_{11})_2$ *iso*	....	156°	40°	
6. $NH(CH_2C_2H_5)_2$	....	....	152°	
7. $C_6H_5NHCH_3$	....	....	126°	
8. $C_6H_5NHC_2H_5$	....	....	boils 285° (110 mm.)	
9. $C_6H_5CH_2NHC_2H_5$	....	158°	57°	
10. $CH_3CONHNHC_6H_5$	....	....	174°	
11. $OC(NHCH_3)_2$	....	....	....	104°–105°*
12. $C_6H_5C(NH_2):NH$	....	Yields compound $C_{19}H_{24}O_4N_2$ 184°*		

The foregoing table gives the type formulas and melting points of all the compounds of camphoroxalic acid and secondary amines which have been prepared hitherto. Those described before the appearance of this paper are marked.* The derivative of symmetrical dimethylcarbamide is included, although it is a derivative of a primary amine, because the parent substance is a secondary amine. Benzamidine may be regarded as being a secondary amine and, therefore, its derivative has also been given.

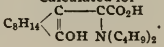
EXPERIMENTAL.

1. *Diisobutylamine.*

Diisobutylamine (2.9 grams = 1 molecule) and camphoroxalic acid (5 grams = 1 molecule) were dissolved in absolute ethyl alcohol and heated on the water bath for fifteen minutes. On cooling, crystals were deposited. These were purified by recrystallization from ethyl acetate, from which they separate in glistening, white needles, melting at 179°–180° with evolution of gas. With alcoholic ferric chloride the violet color, characteristic of the enolic grouping, is produced. Analysis of this compound showed it to be *diisobutylisocamphoformolaminecarboxylic acid.*

Analysis:

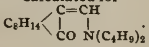
0.2078 gram substance gave 7.4 cc. N at 780 mm. and 21°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll} C & -CCO_2H \\ \Vert & \vert \\ COH & N(C_4H_9)_2 \end{array}\right.$.	Found.
N	3.97	4.08

When this substance is heated above its melting point, water and carbon dioxide are eliminated and a gum is left. This is purified by dissolving it in acetone; it deposited in white plates, melting at 73°–74°. With alcoholic ferric chloride no color reaction is produced. Analysis showed this compound to be *diisobutylcamphoformeneamine.*

Analysis:

0.1043 gram substance gave 4.4 cc. N at 760 mm. and 24°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll} C & =CH \\ \vert & \vert \\ CO & N(C_4H_9)_2 \end{array}\right.$.	Found.
N	4.81	4.61

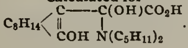
2. *Diamylamine.*

Diamylamine (7 grams = 2 mol.) and camphoroxalic acid (5 grams = 1 mol.) were heated in absolute alcoholic solution on the water bath. On cooling, crystals were deposited which were found to be readily soluble in methyl and ethyl alcohols, ethyl acetate, acetone, ether, and benzene. The compound was purified by recrystallizing from acetone. It separated in white, microscopic crystals melting at 160°. A violet color is produced by dissolving it in alcohol and adding ferric chloride. The compound dissolves in sodium bicarbonate solution with evolution of gas. Analysis showed the substance to be *diamylisocamphoformolaminecarboxylic acid.*

Analysis:

I. 0.1713 gram substance gave 0.4360 gram CO_2 and 0.1644 gram H_2O.

II. 0.2912 gram substance gave 9.4 cc. N at 762 mm. and 24°.

	Calculated for	Found.	
	 $C_8H_{14}\langle C(OH)=C-C(OH)CO_2H\,|\,N(C_5H_{11})_2$.	I.	II.
C	69.23	69.41	. .
H	10.30	10.66	. .
N	3.68	. .	3.54

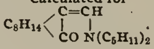
Diamylamine and camphoroxalic acid were also brought together under the following conditions: Camphoroxalic acid (2 grams = 1 mol.) was dissolved in alcohol and with this was mixed an amount of potassium hydroxide nearly sufficient to neutralize it. Diamylamine (1.4 grams = 1 mol.) was now added and the solution concentrated. After this heating, the liquid was rendered barely acid with dilute hydrochloric acid and the crystals which formed were recrystallized from acetone. The purified product was found to be identical with the compound described above.

When this substance is heated above its melting point in a tube connected with a vessel containing baryta water, carbon dioxide is given off, as is shown by the formation of barium carbonate. Water is also eliminated.

The resulting gummy material was treated with benzene and ligroin, and crystals were formed. Recrystallization from acetone and then from ethyl acetate resulted in the deposition of white plates melting at 43°. It was difficult to free these crystals from gum although they were subjected to the action of various solvents a number of times. Analysis indicated that the compound was *diamylcamphoformeneamine.*

Analysis:

0.1715 gram substance gave 6.4 cc. N at 753 mm. and 24°.

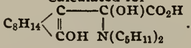
	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll}C & =CH \\ \vert & \vert \\ CO & N(C_5H_{11})_2\end{array}\right.$.	Found.
N	4.40	4.04

3. *Diisoamylamine.*

Diisoamylamine (3.2 grams = 2 mol.) and camphoroxalic acid (2.5 grams = 1 mol.) were dissolved in alcohol and heated till nearly all the solvent was evaporated. Ligroin was then added to the mixture and, on standing, crystals separated. These were purified by recrystallization from acetone, being deposited in white, microscopic crystals melting at 156°. In alcoholic solution a violet color is produced with ferric chloride. The compound dissolves in aqueous sodium bicarbonate solution with evolution of gas. Analysis showed it to be *diisoamylisocamphoformolaminecarboxylic acid.*

Analysis:

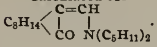
0.1917 gram substance gave 6.4 cc. N at 760 mm. and 25°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll}C & —C(OH)CO_2H \\ \Vert & \vert \\ COH & N(C_5H_{11})_2\end{array}\right.$.	Found.
N	3.68	3.62

When the above compound is heated above its melting point, water and carbon dioxide are eliminated and a gummy mass is left in the tube. This material was purified by recrystallizing from ethyl acetate, being deposited in whitish, rather ill-defined crystals melting at 40°. With alcoholic ferric chloride there is no color reaction. Analysis showed this substance to be *diisoamylcamphoformeneamine.*

Analysis:

0.1400 gram substance gave 5.4 cc. N at 757 mm. and 25°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C=CH\\ \vert \qquad \vert\\ CO\ \ N(C_5H_{11})_2\end{array}\right.$	Found.
N	4.40	4.17

4. *Dibenzylamine.*

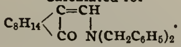
Dibenzylamine (4 grams = 1 mol.), camphoroxalic acid (4.6 grams = 1 mol.), and absolute ethyl alcohol (30 cc.) were heated under pressure, at 130°, for 3 hours, the air in the tube being replaced with illuminating gas. Pressure was noticed in the tube when it was opened and crystals separated on agitating the solution. These were purified by recrystallizing from ethyl acetate and then from alcohol. The compound is deposited in small, glistening, white crystals, melting at 152°.

With alcoholic ferric chloride no color is produced.

Analysis showed this compound to be *dibenzylcamphoformeneamine.* Analysis:

I. 0.1531 gram substance gave 0.4690 gram CO_2 and 0.1182 gram H_2O.

II. 0.1989 gram substance gave 7.0 cc. N at 763 mm. and 25°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C=CH\\ \vert \qquad \vert\\ CO\ \ N(CH_2C_6H_5)_2\end{array}\right.$	Found. I.	Found. II.
C	83.56	83.54	. .
H	8.07	8.57	. .
N	3.90	. .	3.83

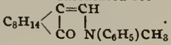
5. *Methylaniline.*

Methylaniline (4.3 grams = 1 mol.), camphoroxalic acid (9 grams = 1 mol.), and benzene (50 cc.) were heated under pressure, at 120°, for 5 hours. Upon evaporating the excess of benzene a gummy mass remained, from which no crystals could be separated by the use of various solvents, the product always depositing from solution as a gum. This gum was, therefore, treated with an aqueous sodium carbonate solution and then extracted with ether. Upon acidifying the carbonate solution with dilute hydrochloric acid, free camphoroxalic acid was precipitated.

The ether solution, when evaporated, deposited crystals which were purified by recrystallization from ethyl acetate, separating in slightly yellow, tetrahedral forms, melting at 126°. With alcoholic ferric chloride no color is produced. Analysis of this compound showed it to be *phenylmethylcamphoformeneamine.* Analysis:

I. 0.1053 gram substance gave 0.3099 gram CO_2 and 0.0864 gram H_2O.

II. 0.1102 gram substance gave 5.3 cc. N at 770 mm. and 24°.

	Calculated for	Found.	
	 $C_8H_{14}<\begin{matrix}C=CH \\ \vert \quad \vert \\ CO \quad N(C_6H_5)CH_3\end{matrix}$	I.	II.
C	80.23	80.26	. .
H	8.61	8.92	. .
N	5.21	. .	5.33

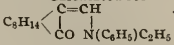
6. *Ethylaniline.*

Ethylaniline (2.15 grams = 1 mol.), camphoroxalic acid (4 grams = 1 mol.), and benzene (40 cc.) were heated under pressure, at 120°, for 5 hours. About half the benzene was then evaporated and ligroin added to the solution. On standing, a gum was deposited. This was then treated with sodium carbonate solution in the manner described in the preceding section, and extracted with ether. When the carbonate solution was acidified with dilute hydrochloric acid, camphoroxalic acid was precipitated.

Upon evaporating the ether solution, a liquid was left and, as it could not be induced to form crystals, it was finally distilled under diminished pressure. Two fractions were obtained. The first, boiling at 140°–145° (110 mm.), was found to be ethylaniline. The second fraction boiled at 285° (110 mm.) and is a deep yellow, viscous liquid. Analysis showed this to be *phenylethylcamphoformeneamine.* Analysis:

I. 0.2247 gram substance gave 0.6580 gram CO_2 and 0.1804 gram H_2O.

II. 0.2253 gram substance gave 10.4 cc. N at 770 mm. and 24.5°.

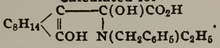
	Calculated for	Found.	
	 $C_8H_{14}<\begin{matrix}C=CH \\ \vert \quad \vert \\ CO \quad N(C_6H_5)C_2H_5\end{matrix}$	I.	II.
C	80.50	79.86	. .
H	8.89	8.92	. .
N	4.95	. .	5.10

7. *Benzylethylamine.*

Benzylethylamine (4.5 grams = 1.5 mols.) and camphoroxalic acid (5 gram = 1 mol.) were mixed and heated in absolute ethyl alcoholic solution on the water bath for 15 minutes. On cooling, crystals were deposited. These were purified by recrystallizing from ethyl acetate and were deposited in fine, white, flocculent crystals melting at 158° with evolution of gas. With alcoholic ferric chloride solution, a violet color is produced. The compound dissolves in sodium bicarbonate solution with evolution of gas. Analysis showed this substance to be *benzylethylisocamphoformolaminecarboxylic acid.* Analysis:

I. 0.1329 gram substance gave 0.3423 gram CO_2 and 0.1007 gram H_2O.

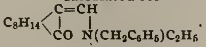
II. 0.1506 gram substance gave 5.5 cc. N at 758 mm. and 24°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C\text{——}C(OH)CO_2H \\ \Vert \qquad \vert \\ COH\ N(CH_2C_6H_5)C_2H_5\end{array}\right.$.	Found.	
		I.	II.
C	70.13	70.24	. .
H	8.13	8.42	. .
N	3.89	. .	3.99

When this compound is heated above its melting point, in a tube connected with a vessel containing baryta water, carbon dioxide is eliminated, as is shown by the formation of barium carbonate in the liquid. Water also is given off. After cooling, a yellow gum was left. As no crystals could be separated by use of ordinary solvents, this gum was treated with sodium carbonate and the solution extracted with ether. A yellow oil was left after evaporating the ether. This solidified on standing. It was redissolved in alcohol and from this solution white crystals are deposited which melt at 57°. With ferric chloride and alcohol no color reaction is produced. Analysis showed the compound to be *benzylethylcamphoformeneamine.*

Analysis:

0.1867 gram substance gave 7.7 cc. N at 760 mm. and 23°.

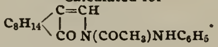
	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C{=}CH \\ \vert \quad \vert \\ CO\ N(CH_2C_6H_5)C_2H_5\end{array}\right.$.	Found.
N	4.72	4.54

8. Acetylphenylhydrazine.

Acetylphenylhydrazine (4.5 grams = 1 mol.), camphoroxalic acid (6.75 grams = 1 mol.), and benzene (30 cc.) were heated under pressure, at 140°–145°, for 14 hours. A considerable pressure was noticed when the tube was opened. When the benzene solution was evaporated, a tarry mass was formed from which no crystals could be separated by the use of various solvents; consequently, the tar was treated with sodium carbonate solution. The part insoluble in the carbonate solution was dissolved in benzene, and ligroin was added. On standing for several days crystals were deposited. These were recrystallized from ethyl acetate several times and then from ethyl alcohol, because the last traces of impurity were difficult to remove. The compound was finally deposited from alcohol in white needles melting at 174°. With alcoholic ferric chloride solution no color reaction is produced. Analysis showed it to be *acetylphenylaminecamphoformeneamine.* Analysis:

I. 0.1110 gram substance gave 0.2970 gram CO_2 and 0.0824 gram H_2O.

II. 0.1074 gram substance gave 9.1 cc. N at 758 mm. and 24°.

	Calculated for 	Found I.	 II.
C	73.07	72.97	. .
H	7.68	8.24	. .
N	8.97	. .	9.24

Some of this compound was heated with potassium hydroxide solution of medium concentration for 3 hours, and then allowed to stand for 40 hours at the room temperature. The solution was now made acid with hydrochloric acid and extracted with ether. The crystals deposited from the ether solution were found to be unchanged material.

A second portion of the substance was then heated with somewhat dilute hydrochloric acid, 2 parts of concentrated acid to 1 part of water, for 3 hours and allowed to stand at the room temperature for 40 hours. The solution was then diluted with water and extracted with ether. From the ether solution, crystals are deposited. They were recrystallized from acetone and came down in glistening, white plates melting at 135°. The compound did not appear to be pure because the melting point was not very sharp, and no concordant analyses could be obtained. Time was lacking for the preparation of larger quantities of this interesting material, but a more complete study of it will be made in the near future.

Secondary Amines with Which no Condensation Compounds Were Formed.

The following acyl derivatives of ortho- and paraminophenol: *Paranitrobenzoylparaminophenol, diparanitrobenzoylparaminophenol, metanitrobenzoylparaminophenol, dimetanitrobenzoylparaminophenol, paranitrobenzoylorthoaminophenol, diparanitrobenzoylorthoaminophenol, metanitrobenzoylorthoaminophenol, dimetanitrobenzoylorthoaminophenol, phenylsulphoneparaminophenol, phenylsulphoneorthoaminophenol, and diphenylsulphoneorthoaminophenol* were heated under pressure, in benzene solution, with camphoroxalic acid to temperatures varying from 165° to 175°, being maintained at these temperatures for several hours, but in no case was there any reaction.

In a paper which we published about a year ago[1] on "Acyl Derivatives of Ortho- and Paraminophenol," we described the preparation and properties of metanitrobenzoylorthoaminophenol and stated that we had prepared it for the first time. Professor Ransom has pointed out to us that he was the first to obtain this compound, as stated in his dissertation.[2]

Paracetoaminophenol was also heated under pressure, in benzene solution, with camphoroxalic acid, at 160°, but no reaction took place.

Benzoylphenylhydrazine and camphoroxalic acid were heated, in benzene solution, at 150° under pressure, and a tarry mass was formed. This was treated with sodium carbonate and the insoluble part dissolved in various solvents, but no definite compound could be isolated. On acidifying the sodium carbonate solution with dilute hydrochloric acid, a small amount of camphoroxalic acid separated.

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[1] THIS JOURNAL, 37, 51 (1907).

[2] Univ. of Chicago, 1900, p. 28.

Benzylphenylhydrazine and camphoroxalic acid were heated in benzene solution, at 140°. A gum formed and this was treated in the same manner as described for the gum from benzoylphenylhydrazine, but no definite compound could be obtained.

Benzylmethylamine and camphoroxalic acid were mixed and heated in absolute ethyl alcohol solution for a short time. The alcohol was then evaporated and a gummy mass was formed, from which no definite compound could be separated.

Phenylmethylhydrazine and camphoroxalic acid were mixed and heated for a short time with absolute methyl alcohol. The solvent was evaporated slowly and a gum was left. This was treated with various solvents but no crystals could be separated from the gum. This latter was then treated with sodium carbonate solution and extracted with ether. The ether solution deposited only a resinous mass, from which no definite compound could be isolated. The sodium carbonate solution was acidified with dilute hydrochloric acid and some camphoroxalic acid separated.

Benzylaniline and camphoroxalic acid were mixed and heated, in benzene solution, for an hour and then the benzene evaporated gradually. A viscid liquid was left, from which no definite compound could be separated. This was then treated with sodium carbonate and extracted with ether. Benzylaniline was left on evaporating the ether, and from the sodium carbonate solution camphoroxalic acid separated on acidifying the liquid with dilute hydrochloric acid.

Phenyl-β-naphthylamine and camphoroxalic acid were heated in benzene solution, under pressure, at 160°, but no reaction whatever took place.

Paraphenylhydrazinesulphonic acid and camphoroxalic acid were heated under pressure, in benzene solution, at 175°, but the two compounds were recovered unchanged.

The action of *benzalaniline* on camphoroxalic acid will be described in a subsequent paper.

Some months after the completion of the work described in the preceding pages, we noticed a paper by O. Dimroth[1] on the interaction of *p*-nitrobenzenediazonium hydroxide and certain ketonic and enolic compounds. After a general discussion of the subject, he suggests the following four equations as representing the possible modes of condensation of these substances:

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[1] Ber. d. chem. Ges., **40**, 2404 (1907).

$$(1)\ \text{—CO}\underset{|}{\text{C}}\text{HH} + \text{HON:NR} \Rightarrow \text{—COCHN:NR};$$

$$(2)\ \text{HO}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{H} + \text{HON:NR} \Rightarrow \text{HO}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{N:NR};$$

$$(3)\ \text{H}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{OH} + \text{HON:NR} \Rightarrow \text{H}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{ON:NR} \Rightarrow \text{HO}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{N:NR};$$

$$(4)\ \text{HO}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{H} + \text{HON:NR} \Rightarrow (\text{HO})_2\overset{|}{\text{C}}\overset{|}{\text{C}}\text{HN:NR} \Rightarrow \text{HO}\overset{|}{\text{C}}\text{:}\overset{|}{\text{C}}\text{N:NR}.$$

The last equation is correct as given here, but is erroneous in Dimroth's paper. Dimroth rejects equation (1) because he failed to obtain condensations with the ketonic compounds which he investigated. The second equation is also discarded because enolic acetyldibenzoylmethane and enolic ethyl diacetylsuccinate, which contain no CH group, condense readily with the diazonium derivative. As between the third and fourth equations, he favors the latter, because only "enols (phenols), but not their ethers or esters, are reactive" in this sense. He states, however, that it is impossible to decide between the two equations until additive compounds of the one or other kind have been prepared and investigated. Dimroth has evidently failed to acquaint himself with the literature on the subject of his investigation, otherwise he would not have overlooked the fact that the senior author alone, and also in conjunction with Alfred Tingle, W. E. Hoffman, Jr., and C. J. Robinson, has described a number of such *addition* compounds, which are termed *camphoformolamine* derivatives, the most interesting being those of camphoroxalic acid with hydroxylamine and *p*-bromphenylhydrazine, respectively. These are, of course, apart altogether from the additive compounds mentioned for the first time in the present communication.

The description of the substances in question, together with full discussions of their constitution and of the bearing which they have on the enolic-ketonic question, are to be found in some eight or ten papers, published at intervals during the past 10 years, chiefly in THIS JOURNAL. The question is dealt with most fully, perhaps, in the paper by Bishop Tingle and Robinson.[1] If Dimroth's reasoning is correect, it follows that the question under consideration was settled some years ago by Bishop Tingle and his colleagues, who regard the fourth of the above equations as the correct representation of the reactions in question, and who have, therefore, always formulated their results in accordance with it. We are glad to receive Dimroth's adhesion to the views which the senior author first recorded many years ago, and although his experimental results are in no way decisive for either method of formulation, yet we welcome them because, in so far as they go, they support the work of the senior author.

The work described in the preceding pages was carried out at the Johns Hopkins University; it will be continued by the senior author at this University.

We desire, in conclusion, to express our grateful thanks to the Trustees of the Warren Research Fund of the American Academy of Arts and Sciences for a grant in aid of the purchase of some of the chemicals employed in this investigation.

MCMASTER UNIVERSITY,
TORONTO, CANADA,
July, 1907.

ON THE AFFINITY CONSTANTS AND CONSTITUTION OF SEVERAL URAZOLES.

[ELEVENTH COMMUNICATION ON THE URAZOLES.]

BY S. F. ACREE AND G. H. SHADINGER.

Phenylurazole must have one of the five following formulas:[2]

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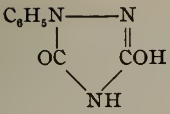
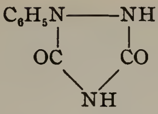
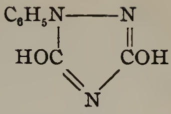
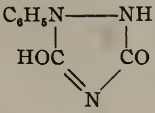
[1] THIS JOURNAL, **36**, 223 (1906).

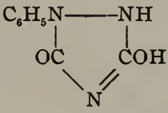
[2] *Ibid.*, **27**, 118; **31**, 185, **32**, 606; **37**, 71, 361; **38**, 1. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.


I.


II.


III.


IV.


V.

It has been proven that it does not exist in solution appreciably as formula V.,[1] and that it seems to react chiefly as formula I. in equilibrium with small amounts of formulas II. and III. and, perhaps, much less of formula IV.

Since both phenylurazole and phenyl-3-thiourazole form salts which, when treated with alkyl halides or alkyl sulphates, are alkylated chiefly in the 2,3 amide group, it seemed probable at the beginning of this investigation that this group is more strongly acid than the 4,5 amide group.

Since, in general, enol groups are stronger acids than keto groups, it seemed probable that the 2,3 group is present in solution largely in the enol form, and the 4,5 group chiefly in the keto form. Corroborative evidence was found in the action of diazomethane upon urazoles, thiourazoles, etc. These reactions showed that the 2,3 amide group of phenylurazole in ether solution is nearly all enol form in equilibrium with a small amount of keto form, while the 4,5 amide group is nearly all keto form in equilibrium with a small amount of enol form. In each case studied, the derivatives of phenylurazole seem to behave in an entirely analogous way.

1-Phenyl-3-thiourazole, however, reacts towards diazomethane in ether solution as if the 2,3 amide group were practically completely enol in structure, and the 4,5 amide group as if it were chiefly keto derivative in equilibrium with a small amount of enol compound.

All of the 1-phenyl-2- or 3-alkylurazoles studied react as if they were nearly completely keto compounds in equilibrium with small amounts of enol derivatives. It has been clearly pointed out, however, in a former article by one of us[1] that the evidence secured by purely chemical means or by physical chemical methods is not to be considered entirely trustworthy.

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[1] Ber. d. chem. Ges., **36**, 3139.

Compounds having a keto structure might be comparatively strong acids, and enol derivatives might be weak acids. It is possible that such elusive tautomeric substances, even though they may exist chiefly as enol form, may react with diazomethane as if they had only the keto structure. This would happen if (1) the keto form reacts more rapidly with the diazomethane than does the enol form, (2) the keto form is in equilibrium with the enol form, and (3) the two forms change into each other very rapidly.

It is perfectly clear, then, that other evidence must be brought to bear on the problem of the constitution of these tautomeric urazoles, and the object of the work presented in this communication was to see what light the application of some of the methods of physical chemistry could throw on the subject.

If this chemical evidence is to be depended upon, a study of the conductivity of these urazoles ought to show that the 2,3 amide group is a very much stronger acid than the 4,5 amide group. The prediction has been fully verified experimentally and the results which were obtained amply confirm the validity of the conclusions drawn from the earlier evidence.

Table A.

Urazoles.	Affinity constants.
1-Phenylurazole	0.000011
1-Phenyl-4-methylurazole	0.000011
1-Phenyl-2-methylurazole	0.000000065
1-Phenyl-3-ethoxyurazole	0.000000043

Table B.

Thiourazoles.	Affinity constants.
1-Phenylthiourazole	0.017
1-Phenyl-4-methylthiourazole	0.017
1-Phenyl-3-ethylthiourazole	0.00000075
1-Phenyl-3-methylthiourazole	0.00000020

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[1] Acree: THIS JOURNAL, **38**, 1.

In Table A. above, it is seen that the affinity constants of phenylurazole and phenyl-4-methylurazole are practically the same. This proves that, as was anticipated, most of the hydrogen and urazole ions of phenylurazole come from the 2,3 enol group and very little from the 4,5 keto group. It was, therefore, predicted that when the 2,3 amide hydrogen is replaced by a radical the affinity constant would fall to a marked extent. This idea has been amply verified, especially when hydrogen is replaced by methyl in the 2 position or by ethyl in the 3 position, the value for the affinity constants falling to about one-half of one per cent of that for phenylurazole. The methyl and ethyl radicals have about the same influence upon the 4,5 amide group.

In Table B. similar results are shown for the thiourazoles. Again the 1-phenyl-4-methyl-3-thiourazole has practically the same affinity constant as the phenyl-3-thiourazole itself. This proves that most of the hydrogen ions come from the 2,3 enol group and that the 4,5 amide (keto) group is a very weak acid. When the hydrogen of the 2,3 amide group of phenyl-3-thiourazole is replaced by the methyl or ethyl radical a marked diminution in strength is shown by the alkylurazole formed. Both radicals affect the affinity constant of the 4,5 amide group to about the same degree, as was the case with phenylurazole. It is interesting to note that by a replacement of the 3-ethoxy and 2-methyl groups by the more negative 3-thioethyl and 3-thiomethyl groups, the affinity constants become from 4 to 15 times as large.

Previous chemical work had led to the conclusion that phenyl-3-thiourazole is a much stronger acid than phenylurazole. Phenyl-3-thiourazole titrates more sharply with alkalis than does the phenylurazole and it is strong enough to color methyl orange red, whereas phenylurazole does not. A comparison of Tables A. and B. shows that the 1-phenyl-3-thiourazole and 1-phenyl-4-methyl-3-thiourazole are 1500 times as strong as the phenylurazole and 1-phenyl-4-methylurazole. This confirmation of the purely chemical evidence by that secured by the use of physical chemical methods is very satisfactory. In order to secure conclusive evidence regarding the constitution and reaction of such tautomeric compounds both methods must be used.

During the time required to read the conductivity of these compounds there seemed to be no tautomeric changes, but, as the writers had already observed while studying certain alkylation reactions by means of titration methods, there was a change of phenyl-3-thiourazole and phenyl-4-methyl-3-thiourazole into the disulphides. See Tables 10 and 12 in Section I., and Table 36 in Section II., in the next article by the writers.

Conductivity Apparatus.

The Kohlrausch method of measuring conductivity with a Wheatstone bridge, a telephone receiver, and an induction coil, was used. The bridge wire was made of "manganin" and was carefully calibrated. The resistance coils were standardized and found to be accurate to 0.04 per cent.

The conductivity cells were of the form used by Jones and Bingham.[1] These cells contained no material soluble in the solvent, prevented evaporation, and protected anhydrous solvents from the moisture of the atmosphere.

The electrodes were coated with platinum black, and then heated in a blast lamp until they became white. This white coating neither absorbs salts nor exerts any oxidizing action.

The sliding contact for determining the zero point was of a special form, as illustrated in Fig. I., having a double contact. The two buttons are pressed down alternately. This can be done quickly, and in this way a much more accurate reading can be made in a shorter time, as the

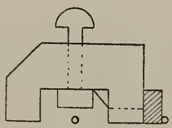

Fig 1. End View

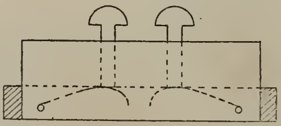

Fig I, Side View

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[1] This Journal, 34, 493.

error involved in having to remember the sound is much less than when the ordinary single contact is used.

Solvents.

Water.—The water was purified by the method of Jones and Mackay[1] and had a conductivity of from 1.8 to 2.3 × 10^{-6} at 25°.

Ethyl Alcohol.—The best commercial article was digested with calcium oxide and distilled through a Linnemann fractionating head. The conductivity was 2 × 10^{-6} at 25°.

Standard Alcoholic Hydrochloric Acid.—The alcohol prepared as above was put into a graduated flask and dry hydrochloric acid gas passed in until a slight excess over the weight required for the standard solution was obtained. The flask was filled to the mark with alcohol and the calculated amount necessary to make the solution of standard strength was then added.[2]

Bath.

The 25° bath was of the usual form, the stirrer being driven by a water motor. An Ostwald regulator was employed, but the gas channel was constricted enough to make the apparatus sensitive to 0.01°. The thermometer was standardized and graduated into tenths of a degree, but could be read easily to within 0.01°. Solutions of the urazoles in water were always made as concentrated as possible and then dilutions made as far as it was practicable to measure the conductivities.

Conductivity Measurements.

In all determinations at least three different resistances were used and the values given are the mean. The constants of the cells were checked at frequent intervals. When not in use, the cells were filled with pure water. A 0.02 normal solution of potassium chloride was used in determining the cell constants. The conductivity of the 0.02 normal solution was taken as 129.7 at 25°. All work was done at 25°.

The μ_∞ of the Sodium Salts and of the Urazole Acids.—The μ_∞ of each sodium urazole was obtained by diluting the solutions until a maximum molecular conductivity was reached. Since the sodium salts of the urazole acid esters are hydrolyzed in dilute solutions, enough of the acid ester itself was added to the solution to suppress this hydrolysis. The conductivity of the urazole acid ester in the presence of its salt is small enough to be neglected, as can be seen from Table 6.

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[1] This Journal, **19**, 91.

[2] Acree and Brunel: *Ibid.*, **36**, 117.

The μ_∞ of the acids and acid esters was obtained by the use of Kohlrausch's law. This value was, on the average, about 355, which is about the same as that for other acids having nearly the same molecular weight.

The affinity constants of the urazoles were then obtained by using Ostwald's formula for the acids and acid esters and Rudolphi's formula for the sodium salts. It was shown in a former article by one[1] of us that the formula

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1K_3)}{(1 + K_3)} = K$$

gives the correct affinity constant for such tautomeric urazole acids. H is the concentration, in gram molecules per liter, of the hydrogen ions, C_{ki} that of the keto anions, C_{ei} that of the enol anions, C_k that of the keto molecular form, C_e that of the enol molecular form, K_1 the affinity constant of the keto tautomer, K_2 that of the enol tautomer, and K_3 the ratio of the amount of keto molecular form to that of the enol molecular form. Since the ionic velocities of the enol and keto anions are approximately the same, the above equation assumes the form of the one used by Ostwald,

$$\frac{\alpha^2}{1 - \alpha} = \frac{\mu^2_v}{\mu_\infty(\mu_\infty - \mu_v)} = KV.$$

The same reasoning shows that the Rudolphi dilution equation holds for the salts of tautomeric acids or bases.

EXPERIMENTAL.

Phenylurazole.—This was made by the method of Acree.[2] One hundred grams of phenylhydrazine gave 100 grams of phenylurazole which, after recrystallization from alcohol, melted at 265° to 267° without decomposition. This was crystallized twice from alcohol, and water solutions were made for the conductivity measurements.

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[1] Acree: This Journal, **38**, 12.

[2] *Ibid.*, **27**, 126.

Sodium Salt of Phenylurazole.—Fifteen grams of the pure phenylurazole were heated for several hours in conductivity water in a beaker with the theoretical weight of sodium bicarbonate. Upon evaporating the solution to a small volume and cooling it, a white precipitate was formed. This was crystallized three times from distilled water and twice from conductivity water and dried in a desiccator over sulphuric acid.

The following method of analysis was followed for all sodium salts: About 0.3 gram was weighed into a platinum crucible and 3 cc. dilute sulphuric acid were added. This mixture was evaporated and the residue was ignited in a Rogers burner; the process was then repeated and the product was weighed as sodium sulphate.

Analysis:

0.2519 gram anhydrous substance gave 0.0869 gram Na_2SO_4.
6.6233 gram substance lost 1.1528 gram H_2O at 120°.

	Calculated for $C_8H_6O_2N_3Na$.	Found.
Na	11.54	11.17

	Calculated for $C_8H_6O_2N_3Na.2H_2O$.	Found.
$2H_2O$	17.25	17.40

Table I.—Sodium 1-Phenylurazole. $\mu_\infty = 80.44$.

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}$.
16	57.77	0.719	0.447
32	60.04	0.747	0.388
64	62.40	0.775	0.335
128	65.05	0.809	0.302
256	67.72	0.841	0.280
512	70.00	0.870	0.258
1024	81.58	1.014	
2048	79.28	0.985	

The maximum molecular conductivity of the acid is obtained as follows: By the law of Kohlrausch $C+A = 80.44$ for the sodium salt; therefore $A = 80.44 - 49.2 = 31.24$, and the μ_∞ of the acid is 31.24+325 or 356.24.

Table II.—1-Phenylurazole. $\mu_\infty = 356.24$.

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)} V$.
512	26.36	0.0740	0.0000115
1024	36.30	0.102	0.0000118
2048	47.77	0.134	0.0000102
4096	65.38	0.183	0.00000984
8192	82.25	0.230	0.00000946
16384	125.55	0.352	0.0000121

$K = 0.000011$

Sodium Salt of 1-Phenyl-2-methylurazole.—Two grams of phenyl-2-methylurazole in water were treated with the theoretical weight of pure sodium bicarbonate and heated some hours in a beaker to expel the carbon dioxide. When the solution was evaporated to a small volume and cooled, the salt precipitated out. It was recrystallized three times from conductivity water.

Analysis:

0.2745 gram of anhydrous substance gave 0.1005 gram Na_2SO_4.

0.7227 gram substance gave 0.1445 gram H_2O at 120°.

	Calculated for $C_9H_8O_2N_3Na$.	Found.
Na	10.79	10.85

	Calculated for $C_9H_8O_2N_3Na.3H_2O$.	Found.
$3H_2O$	20.20	19.99

Table III.—Sodium 1-Phenyl-2-methylurazole. $\mu_\infty = 69.2$.

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}$.
64	59.07	0.8576	0.622
128	61.26	0.885	0.603
256	62.76	0.907	0.552
512	64.37	0.930	0.548
1024	66.10	0.955	0.637
2048	71.52	1.033	
Hydrolysis suppressed with molecular amount of 1-phenyl-2-methylurazole.			
2048	69.255	1.000	

The maximum molecular conductivity of the acid is obtained as follows: $C+A = 69.2$ for the sodium salt; therefore, $A = 69.2 - 49.2 = 20$, and the μ_∞ of the acid is $20+325$ or 345.

1-Phenyl-2-methylurazole.[1]—Twenty-four grams of phenylurazole were dissolved in a small amount of water containing one molecular proportion of sodium hydroxide. Two molecules of dimethyl sulphate, which had been shaken with alkali to remove the free acid, were added and the whole shaken one-half hour. The precipitate was recrystallized three times from distilled water, hydrolyzed with hydrochloric acid to decompose any methoxy derivative, extracted with chloroform to remove the phenylurazole, and recrystallized from conductivity water. Four grams of pure product were obtained which melted at 185°.

Table IV.—1-Phenyl-2-methylurazole. $\mu_\infty = 345$.

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)V}$.
128	1.007	0.00291	0.0000000668
256	1.452	0.00420	0.0000000694
512	1.849	0.00535	0.0000000564
1024	2.527	0.00732	0.0000000664
2048	6.894	0.0199	(0.000000197)
4096	8.155	0.0237	(0.000000140)
			$K = 0.000000065$

Sodium Salt of 1-Phenyl-3-ethoxyuzazole.—This was prepared and purified in a manner similar to that employed for the preparation of the sodium salts spoken of above.

Analysis:

0.2999 gram of anhydrous substance gave 0.0883 gram Na_2SO_4.

	Calculated for $C_{10}H_{10}O_2N_3Na$.	Found.
Na	10.12	10.70

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[1] For a description of the derivatives of phenylurazole used in this work, see the article by Acree: This Journal, **38**, **1**.

Table VI.—Sodium 1-Phenyl-3-ethoxyurazole. $\mu_\infty = 82$.

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}$.
32	59.13	0.721	0.329
64	61.96	0.755	0.292
128	64.25	0.783	0.250
256	65.22	0.795	0.193
512	67.33	0.821	0.200
1024	69.72	0.850	0.150
4096	77.18	0.941	0.235

Suppression of hydrolysis by an equal amount of 1-phenyl-3-ethoxyurazole.

V.	μ_v.	α.
4096	82.14	1.001
8192	81.62	0.995

The maximum molecular conductivity of the acid is obtained as follows: $C + A = 82$ for the sodium salt; therefore $A = 82 - 49.2 = 32.8$, and the μ_∞ of the acid is $32.8 + 325$ or 357.8.

1-Phenyl-3-ethoxyurazole.—Much difficulty was experienced in obtaining this ester in large quantities by the alkylation of phenylurazole salts, and several methods were tried before a satisfactory one was found.

1. *Alkylation Experiments in Ether as a Solvent.*—Seventy-five grams of phenylurazole and a drop of phenolphthalein solution were titrated with a solution of potassium hydroxide. The solution was warmed and one molecular portion of silver nitrate in a little water was added with constant stirring. The silver salt was white when first formed, but soon turned dark. When washed with alcohol and ether and dried, it weighed 112 grams. Forty-five grams of this silver salt, suspended in 400 cc. of ether, and 1.5 molecules of ethyl iodide (37.5 grams) were boiled two days in a liter flask under a return condenser. The silver residue was filtered off and the ether filtrate was treated in the cold with a slight excess of dilute potassium hydroxide solution to extract the 1-phenyl-3-ethoxyurazole. This alkaline extract, when acidified with dilute sulphuric acid, gave a white precipitate of phenylurazole, 1-phenyl-3-ethoxyurazole, 1-phenyl-2-ethylurazole, and perhaps other products, and more of the ethyl esters were obtained by extracting the filtrate with ether or chloroform. Recrystallization of the precipitate from a large amount of 50 per cent alcohol gave pure white, needlelike crystals which melted from 150° to 200°. When this precipitate was treated with chloroform and filtered, a small quantity of phenylurazole was left as an insoluble residue. The chloroform filtrate was evaporated and the residue was crystallized from 50 per cent alcohol. Crystals of pure 1-phenyl-3-ethoxyurazole were obtained which melted at 152° and weighed 1.2 grams. The filtrate from the 1-phenyl-3-ethoxyurazole was evaporated and it then gave 1.8 grams of crystals melting at 75° to 80°, which were probably largely 1-phenyl-2-ethylurazole. The ether solution from which the 1-phenyl-3-ethoxyurazole and 1-phenyl-2-ethylurazole were extracted retained the 1-phenyl-3,5-diethoxyurazole. The ether was evaporated off and a yellow oil was obtained which solidified on standing. This oil weighed 3.2 grams. When it was dissolved in alcohol and water was added, fine white needles were precipitated. The 1-phenyl-3,5-diethoxyurazole, when crystallized twice, as before, melted at 52°. The yield was 2.5 grams. This method was repeated twice and in both cases the same poor yields were obtained.

2. *Shaking the Silver Salt and Ethyl Iodide in Cold Ether.*—The same quantities of reagents were used as in the preceding experiment, but were shaken in a stoppered bottle three days. When the reaction product was treated as before the yield was 1.4 grams of 1-phenyl-3-ethoxyurazole (melting point 147° to 149°), 2.2 grams of low melting product (melting point 68° to 74°), and 3.6 grams of crude 1-phenyl-3,5-diethoxyurazole.

3. *Silver Phenylurazole and Pure Ethyl Iodide in the Cold.*—Ten grams of silver salt were shaken four days in a bottle with 50 grams of ethyl iodide. When the reaction product was treated as before, the yield was 0.1 gram 1-phenyl-3-ethoxyurazole, 0.5 gram low melting material (melting point 68° to 76°), and 0.7 gram crude 1-phenyl-3,5-diethoxyurazole. The yields for these three methods are about the same.

4. *Silver Phenylurazole and Pure Ethyl Iodide in Sealed Tubes.*—Fifty grams of the silver salt were put in two large Carius tubes and enough ethyl iodide (320 grams) was added to make a soft

mush. The tubes were heated two days at 50° and two days at 75°. When the reaction product was treated as before it gave 4 grams of 1-phenyl-3,5-diethoxyurazole in good condition, although it had to be crystallized first from pure alcohol. The fraction which should have been 1-phenyl-3-ethoxyurazole contained so little of this that it could not be separated from the 1-phenyl-2-ethylurazole by the ordinary methods. This fraction melted at 65° to 85°.

5. *Silver Phenylurazole and Ethyl Iodide in Ether in Sealed Tubes.*—Seventy-five grams of the silver salt were put into two tubes with two molecular proportions of ethyl iodide, and three or four times the volume of ether was then added. These two tubes were heated three days at 75°, when an accident caused the loss of one tube. The contents of the other were treated as before and gave 4 grams of 1-phenyl-3,5-diethoxyurazole in good condition, but the other product melted low, as before. This low melting material was titrated with 55 cc. of 0.1 normal sodium hydroxide solution and the urazoles were fractionally precipitated with 0.1 normal sulphuric acid. Eleven cc. of acid were used for each fraction. The first precipitate melted at 100° to 150°; the second at 80° to 125°; the third, fourth, and fifth at 72° to 95°. The first fractions were recrystallized three times from alcohol and gave 2 grams of 1-phenyl-3-ethoxyurazole, which melted at 151° to 152°. This last method seems the best of the five given.

The unchanged phenylurazole left with the silver residue can be recovered by saturating the required amount of potassium hydroxide solution with hydrogen sulphide and digesting the silver salt with the solution in the cold several hours. When the silver sulphide is filtered off and the filtrate is boiled to remove hydrogen sulphide, and acidified, the phenylurazole precipitates out in pure condition.

6. *Preparation and Hydrolysis of 1-Phenyl-3,5-diethoxyurazole.*—Thirty grams of phenylurazole were converted into disilver phenylurazole[1] by dissolving the phenylurazole in somewhat more than one molecular proportion of potassium hy-

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[1] Acree: This Journal, **38**, 1; Ber. d. chem. Ges., **36**, 3146.

droxide solution, then adding nearly one molecular proportion of silver nitrate in solution, and then, alternately, solutions of potassium hydroxide and silver nitrate in separate portions until two molecular proportions of each had been used. The silver salt was prepared in a two-liter bottle which was shaken violently during the experiment. Only small quantities of the reagents should be added each time, and the bottle must be shaken *well* after each addition. The bottle was then agitated for several hours in a machine. After standing overnight, the gelatinous material was collected so that it could be filtered. It was dried in the air on porous plates. Heating, to hasten drying causes decomposition. The yield is always quantitative. The salt was then put in a flask with 500 cc. of ether and three molecular proportions of ethyl iodide and boiled three days. After filtering off the silver salts, the filtrate was extracted with potassium hydroxide solution. When the alkaline solution was acidified, it gave 1.2 grams of yellowish crystals melting at 66° to 73°.

After the ether was distilled off, the yellow oil which was left solidified. After crystallizing this solid from 95 per cent alcohol, 9.5 grams of 1-phenyl-3,5-diethoxyurazole were obtained, which melted at 52° to 53°. From the filtrate 5.2 grams of the same compound melting at 49° to 52° were obtained. It was found that, when the pure 1-phenyl-3,5-diethoxyurazole was heated in a sealed tube one hour at 85° with exactly one molecular proportion of hydrogen chloride in alcohol, the 5-ethoxy group was hydrolyzed quantitatively and pure 1-phenyl-3-ethoxyurazole was left. When the impure fraction, melting at 49° to 52°, was hydrolyzed with alcoholic hydrochloric acid, it gave 1-phenyl-3-ethoxyurazole which, after crystallization from 50 per cent alcohol, melted at 150° to 151°. This last method is the most satisfactory one used for the preparation of 1-phenyl-3-ethoxyurazole.

The sample of 1-phenyl-3-ethoxyurazole used in the conductivity measurements was recrystallized several times from pure 50 per cent alcohol.

Table VII.—1-Phenyl-3-ethoxyurazole.

$\mu_\infty = 357.8.$

$V.$	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)V}$
1024	2.106	0.00589	0.0000000340
2048	3.470	0.00961	0.0000000463
4096	4.451	0.0124	0.0000000382
8192	7.072	0.0198	0.0000000487
			$K = 0.000000043$

1-Phenyl-4-methylurazole.—This was made by the hydrolysis of 1-phenyl-3-ethoxy-4-methylurazole with hydrochloric acid.[1] This latter ester was made by treating 8 grams of 1-phenyl-3-ethoxyurazole with one molecular proportion of potassium hydroxide in 50 cc. of water and shaking the solution one hour with 1.5 molecular proportions of neutral dimethyl sulphate. Potassium hydroxide in solution was added from time to time to keep the solution alkaline. The product soon crystallized out. It was found that the yield is always much better if the solution is warmed before shaking. When recrystallized three times from alcohol containing a small amount of potassium hydroxide, the 1-phenyl-4-methyl-3-ethoxyurazole melted at 96°. Four grams of this ester were evaporated three times with concentrated hydrochloric acid and the residue was crystallized from alcohol. Three grams of 1-phenyl-4-methylurazole, melting at 225°, were obtained.

Table VIII.—1-Phenyl-4-methylurazole.

$\mu_\infty = 355.$

$V.$	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)V}$
512	26.98	0.076	0.0000122
1024	37.49	0.105	0.0000121
2048	46.76	0.132	0.0000136
4096	61.94	0.174	0.00000900
8192	74.67	0.210	(0.00000683)
			$K = 0.000011$

Sodium Salt of 1-Phenyl-4-methylurazole.—This salt was made by the method used for preparing the other sodium salts.

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[1] Acree: This Journal, 38, 1.

Table IX.—Sodium Salt of 1-Phenyl-4-methylurazole.

$\mu_\infty = 82.81.$

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}$.
64	55.80	0.674	0.174
128	62.19	0.751	0.200
Hydrolysis suppressed with 0.25 molecule of 1-phenyl-4-methylurazole.			
256	61.17	0.739	0.130
512	63.99	0.773	0.116
1024	63.80	0.770	0.0808
2048	68.07	0.822	0.0839
4096	71.37	0.862	0.0594
8192	82.81	1.00	

1-Phenyl-3-thiourazole.—This was made by Acree's method.[1] Ethyl 1-phenylthiosemicarbazide-1-carboxylate was extracted in a Soxhlet apparatus with alcohol and consequently the phenyl-3-thiourazole was obtained in excellent condition. For further purification it was dissolved in an excess of potassium hydroxide, heated two hours, and again precipitated by the addition of hydrochloric acid. When it was recrystallized twice from alcohol, it melted at 192° to 193°. The μ_∞ for all of the thiourazoles used in this work was assumed to be 355, which is certainly not far from the correct value. An error of even 10 conductivity units makes no appreciable error in the values of the affinity constants.

Table X.—1-Phenyl-3-thiourazole.

$\mu_\infty = 355.$

V.	μ_v.	α.	$K = \frac{\alpha^2}{(1-\alpha)V}$.
64	226.41	0.637	0.0175
128	271.68	0.765	0.0194
256	292.78	0.824	0.0151
Disulphide was formed very rapidly.			
512	305.96	0.861	(0.0105)
1024	295.43	0.822	(0.00403)
2048	143.30	0.403	
			$K = 0.017$

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[1] **Ber. d. chem. Ges., 36, 3151.**

Sodium Salt of 1-Phenyl-3-thiourazole.—This salt was made by dissolving the theoretical weight of pure sodium bicarbonate in water, adding the 1-phenyl-3-thiourazole, and boiling the solution to expel the carbon dioxide. The solution was evaporated to dryness and the residue was heated two hours in an air bath. At the end of this time, all water of crystallization had been driven off and the weight was constant.

Table XI.—Sodium Salt of 1-Phenyl-3-thiourazole.

$\mu_\infty = 77.35.$

$V.$	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}.$
16	41.09	0.501	0.126
32	43.03	0.525	0.129
64	44.62	0.570	0.0946
128	49.09	0.599	0.0791
256	48.19	0.588	0.0525
512	50.78	0.619	0.0446
1024	64.95	0.728	0.0948
2048	58.96	0.719	0.0408
4096	67.72	0.826	0.0445
8192	77.35	1.00	

1-Phenyl-4-methyl-3-thiourazole.—This urazole derivative was made by the method suggested by Acree.[1] The 1-phenyl-4-methylthiosemicarbazide was made from phenylhydrazine and methyl mustard oil.[2] The ethyl 1-phenyl-4-methylthiosemicarbazide-1-carboxylate was made from 1-phenyl-4-methylthiosemicarbazide and ethylchlorcarbonate by Acree's method.

The reagents for making the ester were dissolved in chloroform and the solution was heated one day. When the reaction mixture was cooled, the ester which crystallized out melted at 196°. The chloroform was distilled off and the residue solidified. At first it melted slightly under 100°, but when recrystallized twice from alcohol, its melting point was 102° to 103°. This substance was not identified.

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[1] Acree: Ber. d. chem. Ges., **36**, 3154.

[2] Dixon: J. Chem. Soc., **57**, 261. Busch: Ber. d. chem. Ges., **37**, 2332. Marckwald: *Ibid.*, **25**, 3107.

Table XII.—1-Phenyl-4-methyl-3-thiourazole.

$\mu_\infty = 355.$

V.	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)V}.$
256	299.72	0.844	0.0178
512	309.66	0.872	0.0116
Disulphide was formed very rapidly.			
1024	269.18	0.758	(0.00232)
2048	283.18	0.797	(0.00146)
4096	281.49	0.792	(0.000741)
8192	292.56	0.823	(0.000471)
			$K = 0.017$

1-Phenyl-3-methylthiourazole.[1]—Five grams of phenylthiourazole were neutralized with normal potassium hydroxide solution. This solution was diluted with two-thirds of its volume of alcohol and 1.15 molecular proportions of methyl iodide, and was then boiled fifteen minutes. The new material crystallized out when the solution was cooled. This ester was purified by crystallizing it from water, from alcohol containing a little methyl iodide, from absolute alcohol, and then from conductivity water. It weighed 3.5 grams and melted at 174° to 175°.

Table XIII.—1-Phenyl-3-methylthiourazole.

$\mu_\infty = 355.$

V.	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)V}.$
1024	4.02	0.0113	0.000000126
2048	5.37	0.0151	0.000000113
4096	10.06	0.0283	0.000000202
16384	25.07	0.0706	0.000000327
			K = 0.0000002

Sodium Salt of 1-Phenyl-3-methylthiourazole.—This was made and treated like the preceding sodium salts.

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[1] Acree: Ber. d. chem. Ges., **36**, 3151.

Table XIV.—Sodium Salt of 1-Phenyl-3-methylthiourazole.

$\mu_\infty = 86.95.$

$V.$	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}.$
64	63.63	0.731	0.249
128	70.29	0.815	0.318
256	69.07	0.794	0.191
512	73.54	0.845	0.205
1024	72.92	0.838	0.136
2048	82.04	0.943	0.348
4096	84.61	0.973	0.388
8192	86.95	....	.....

1-Phenyl-3-ethylthiourazole.[1]—The method of preparation and purification was entirely similar to that given for 1-phenyl-3-methylthiourazole. Four grams of pure ester, melting at 137° to 138°, were obtained from 5 grams of phenylthiourazole.

Table XV.—1-Phenyl-3-ethylthiourazole.

$\mu_\infty = 355.$

$V.$	$\mu_v.$	$\alpha.$	$K = \frac{\alpha^2}{(1-\alpha)V}.$
2048	10.98	0.0309	0.000000483
4096	19.29	0.0943	0.000000762
16384	42.54	0.119	0.000000996
			$K = 0.00000075$

Barium Salt of 1-Phenyl-3-thiourazole.—This was made by titrating 2 grams of the 1-phenyl-3-thiourazole with the theoretical amount of standard barium hydroxide solution, evaporating the solution and drying the salt as before.

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[1] Acree: Ber. d. chem. Ges., **36**, 3151.

Table XVI.—Barium Salt of 1-Phenyl-3-thiourazole.

See errata p. 823

$\mu_\infty = 103.19.$

V.	μ_v.	α.	K= ~~X~~ $\frac{\alpha^2}{(1-\alpha)\sqrt{V}}$.
64	77.04	0.746	0.274
128	87.98	0.852	0.435
256	88.52	0.857	0.323
512	93.89	0.909	0.406
1024	94.54	0.916	0.313
2048	99.80	0.935	0.318
4096	101.18	0.961	0.275
8192	103.19	....	....

1-Phenyl-3-ethoxy-4-methylurazole.—See page 138, under 1-phenyl-4-methylurazole.

On the Basic Properties of Some Urazole Esters.

In order to see if some of the urazole esters are weak bases and unite to some extent with hydrochloric acid in alcoholic solutions,[1] some conductivity measurements were made on alcoholic hydrochloric acid solutions to which varying amounts of the ester were added.

The conductivity of 0.1 normal alcoholic hydrochloric acid at 25° was found to be 21.221.[2] The data available show that the conductivity in absolute alcohol at infinite dilution of a salt having the molecular weight of those probably formed in the experiments below referred to is from one-third to one-fourth that of hydrochloric acid in equal concentration in alcohol. Therefore, the conductivity of the hydrochloride of the 1-phenyl-3-ethoxyurazole and of the other esters was taken to be one-fourth that of the 0.1 normal hydrochloric acid, or 5.302.

The total lowering of conductivity which could be produced if all the base were changed to hydrochloride would then be 21.211 — 5.302 = 15.909. The percentage of salt formed as successive amounts of base were added is found by dividing the lowering in conductivity produced by the total lowering possible. The data do not take into consideration the small change in volume produced by adding the urazole ester. If the data were sufficiently accurate, the affinity constants of the bases could be calculated.

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[1] Acree and Johnson: **This Journal, 38,** 336.

[2] Wildermann: Z. physik. Chem., **14,** 231, 247. Scholl: *Ibid.*, **14,** 701. Sill: *Ibid.*, **51,** 595. Walden: *Ibid.*, **54,** 129. Godlewski: J. Chim. Phys., **3,** 393.

Table XVII.—1-Phenyl-3-ethoxyurazole in 0.1 N Alcoholic HCl.

Amount of ester added to 25 cc. 0.1 N alcoholic HCl.	μv.	Per cent of salt formed.
0 molecule	21.22	....
0.25 "	20.83	3.74
0.50 "	20.50	4.44
0.75 "	20.13	6.76
1.00 "	19.81	8.77
1.25 "	19.42	11.26
1.50 "	19.19	12.69
1.75 "	18.88	15.24
2.00 "	18.47	17.15

Table XVIII.—1-Phenyl-3,5-diethoxyurazole in 0.1 N Alcoholic HCl.

Amount of ester added to 25 cc. alcoholic HCl.	μv.	Per cent of salt formed.
0.25 molecule	20.82	2.46
0.50 "	20.46	4.71
0.75 "	20.13	6.75
1.00 "	19.81	8.77
2.00 "	18.39	17.69
3.00 "	17.24	24.94
4.00 "	16.15	31.78

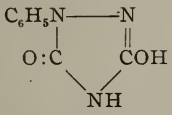
Table XIX.—1-Phenyl-3-ethoxy-4-methylurazole in 0.1 N Alcoholic HCl.

Amount of ester added to 25 cc. alcoholic HCl.	μv.	Per cent of salt formed.
0.25 molecule	21.04	1.04
0.50 "	20.74	2.92
1.00 "	20.13	6.75
2.00 "	19.01	13.79

Conclusions.

The affinity constant of the 2,3 amide group of phenylurazole and of 1-phenyl-4-methylurazole is 0.000011, while that of 1-phenyl-3-thiourazole and 1-phenyl-4-methyl-3-thiourazole is about 1500 times as great, or 0.017. The affinity constant of the 4,5 amide group of the 2-alkyl and 3-alkoxy derivatives of phenylurazole is about 0.00000005, whereas the corresponding derivatives of 1-phenyl-3-thiourazole are several times as strong.

It has therefore been shown by the use of physical chemical and organic methods that those urazoles which seem to have the enol structure have much larger affinity constants than those urazoles which are apparently keto compounds. New evidence has thus been produced in favor of the view that phenylurazole and phenyl-3-thiourazole are tautomeric compounds which exist in solution chiefly in the two forms represented by the formulas



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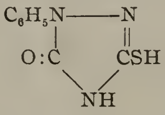

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Johns Hopkins University,
June 10, 1907.

A REPLY TO JULIUS STIEGLITZ'S "NOTE[1] ON THE ARTICLE ENTITLED 'STUDIES IN CATALYSIS'[2] BY S. F. ACREE."

By S. F. Acree.

So many of the statements in Mr. Stieglitz's note are at variance with the facts, as I see them, that I feel it to be my duty to myself and to some of my colleagues to present the following statement "in the interest of the question of priority and of historical truth."

In answer to Mr. Stieglitz's statement that (p. 744) "In my address..........the leading ideas of the theory of catalysis, as now put forth again by Acree without due acknowledgment, were already presented," and that (p. 745) "there is not one single new principle presented in Acree's paper,"

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[1] This Journal, 38, 743.

[2] Acree and Johnson: *Ibid.*, 38, 258.

I shall discuss historically the work of various chemists and *their leading ideas* of the following three fundamental principles believed, until recent years, to apply to catalysis:

(1) The catalyzer seems to act by its simple presence.

(2) The catalyzer affects the velocity constant directly in proportion to the concentration of the catalyzer.

(3) A change in the concentration of the catalyzer does not change the equilibrium point in reversible reactions.

(A) Mr. Stieglitz says (p. 744): "In that address, the first vital and decisive step was taken to depart from the old idea that....the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components. '....The most fundamental fact concerning acids was recalled, the fact that they have the power to form *salts* with bases and oxides. ....' We.....could *prove our point that the acceleration is......due to salt and ion formation.*"

I wish to point out now that every one of these fundamental assumptions, AND ESPECIALLY STIEGLITZ'S KEYNOTE, ACCELERATION THROUGH SALT AND ION FORMATION, *had already been made by Kastle,[1] Euler,[2] Acree,[3] Bredig,[4] and Lapworth,[5] and that Stieglitz advanced them again as his own without once stating that his ideas were not new. Acree and Johnson gave full credit[6] to all of these colleagues and to Stieglitz for their ideas and work. Furthermore, the discovery that the second and third laws of catalysis do not hold in all catalytic reactions was first worked out theoretically by myself and experimentally by Johnson, and also independently by Abel[7] and Euler,[8] and was not even hinted at or discussed in any phase by Stieglitz.*

(1) In their article on Catalysis, J. H. Kastle and J. C. W.

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[1] THIS JOURNAL, **19**, 894. P. Am. Assn. Adv. Sci., **47**, 238. Professor Kastle kindly sent me his original manuscript, from which I give quotations.

[2] Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356. Z. physiol. Chem., **52**, 146.

[3] Acree and Hinkins: THIS JOURNAL, **28**, 370.

[4] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528.

[5] See Mellor's Statics and Dynamics, pp. 289, 335, 338, 339, 342.

[6] Acree and Johnson: THIS JOURNAL, **38**, 299, 300, 301.

[7] Z. Elek. Chem., **13**, 555.

[8] Z. physiol. Chem., **52**, 146.

see errata p. 223.

Frazer presented the following views "as the result of our studies on the hydrolysis of sulphonic esters especially":

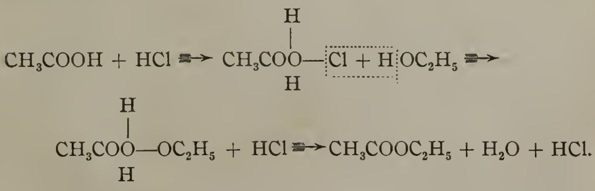
"First, that the catalytic changes involved in etherification, the hydrolysis of ethereal and metallic salts and acid amides, and the inversion of cane sugar and the similar compounds by acids, are essentially the same in kind.

"Secondly, That hydrolysis and etherification are always preceded by the formation of an unstable addition product (Kastle's salt) of the substance undergoing the catalysis and the acid causing the same; and that it is the decomposition of this unstable addition product by water or alcohol that gives the ultimate products of the catalysis.

"Thirdly, That this unstable addition product is produced by the combination of the ions of the acid causing the catalysis with the anhydride or oxide-like oxygen or element of the compound undergoing the change.

"This hypothesis necessarily involves the idea of the quadrivalence of the oxygen atom."

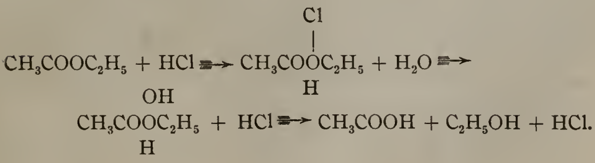
Kastle represented the formation of the ester from acetic acid, alcohol, and hydrochloric acid, as taking place as indicated below:



$$CH_3COOH + HCl \rightleftharpoons CH_3CO\underset{H}{\overset{H}{O}}\text{—}\boxed{Cl + H}OC_2H_5 \rightleftharpoons$$

$$CH_3CO\underset{H}{\overset{H}{O}}\text{—}OC_2H_5 + HCl \rightleftharpoons CH_3COOC_2H_5 + H_2O + HCl.$$

For the hydrolysis of ethyl acetate he gave these expressions:



$$CH_3COOC_2H_5 + HCl \rightleftharpoons CH_3CO\underset{H}{\overset{Cl}{O}}C_2H_5 + H_2O \rightleftharpoons$$

$$CH_3CO\underset{H}{\overset{OH}{O}}C_2H_5 + HCl \rightleftharpoons CH_3COOH + C_2H_5OH + HCl.$$

Although, then, Kastle and Frazer had, in 1898, advanced *the vital points* of Stieglitz's paper, Stieglitz did not acknowledge their priority in the matter.

(2) Mr. Stieglitz's "*our* point that the acceleration.....is due to salt and ion formation" was proposed by Euler[1] in 1901, three years before Mr. Stieglitz's paper appeared. But Mr. Stieglitz did not refer to Euler, who said: "All of these catalytic phenomena....depend upon the increase or decrease of one or more of the substances entering into the (noncatalyzed) reaction; or, by applying electro-chemical principles to all chemistry, they depend upon the increase of the reacting ions." Mellor, in his "Statics and Dynamics," says: "Euler defines a catalytic agent as *a substance which modifies the velocity of chemical reactions by changing the concentration of the ions of the reacting substances.*"

Further, Euler has recently said:[2] "I believe that I have found new proof for my former ideas on catalytic reactions. The compound formed by the ester, or cane sugar, and the mineral acid, which is really the reacting (active) molecule or ion undergoing hydrolysis, has been detected or measured in the catalytic hydrolysis of glycine anhydride. On the other hand, experiments have shown that racemic tartaric acid esters are saponified asymmetrically by optically active acids, a result that can hardly be interpreted otherwise than by the assumption that the compounds formed by the union of the optically active catalyzers, acids, with the two optical opposites, esters, differ in concentration and reactivity."

(3) The writer had been engaged in research work two years before going to Chicago. He began the independent study of catalysis in 1899 by collaborating with Hinkins on the reversible formation and hydrolysis of esters by enzymes and bacteria, and by investigating the formation and reactions of urazole esters. Our idea that *catalyzers accelerate such reactions through double-compound or salt formation* was expressed[3] by the sentence (p. 372): "Hence we are very

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[1] See Z. physik. Chem., **36**, 644.

[2] Z. physiol. Chem., **52**, 146. See also pp. 147–152.

[3] Acree and Hinkins: This Journal, **28**, 370. A number of papers have appeared in various dental journals.

sure that if any changes take place according to the above equation, *the enzyme must take part in the reaction or act as a catalytic agent*," and by the definite use (p. 372) of *enz.* $C_6H_{11}O_5Ac$ (enzyme-ester salt!) and *enz.* $C_6H_{11}O_5OH$ (enzyme-glucose salt!) in our equations. Following this idea, we showed that such ester salts (see equation, page 372) can be formed and also hydrolyzed, and consequently that the assumption of such salts leads to the experimental facts in reversible reactions. We showed further that the equilibrium point produced by enzymes is different from the *natural one* produced by acids, as has been again demonstrated by Bodenstein errata 123 and Dietz;[1] ~~that the velocity of the hydrolysis of esters by enzymes is different from the *natural one* produced by acids, as has been also shown by Bodenstein and Dietz~~; and that the velocity of the hydrolysis of esters by enzymes is proportional to the concentration of the enzyme, just as in the catalysis by acids (p. 376). All of these facts were in harmony with our idea that the basic and acid groups of the enzymes cause salt formation and decomposition. Stieglitz was aware of our independent ideas and of our results, worked out in the Columbus Memorial Laboratory in Chicago and published two years before his article, but he failed to credit us with priority in these ideas.

(4) It seems to me that Mr. Stieglitz deserves credit, not for the idea (Kastle's) of salt formation and its consequences, but for showing clearly for the first time (p. 745) "that the simple application of our common laws of equilibrium to the proved fundamental idea (Kastle's)[2] of salt formation led, mathematically and chemically, directly to the three" so-called laws of catalysis. But even Mr. Stieglitz's keynote or "point that the acceleration....is, as a matter of experiment, due to salt and ion formation" had already been proved quantitatively in a similar case of catalysis by Bredig and Walton,[3] and published in January, 1903, or about eighteen months

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[1] Z. Elek. Chem., **12**, 605. Dietz: Dissertation, Leipzig.

[2] My words.

[3] Z. Elek. Chem., **9**, 118. See also *Ibid.*, **10**, 586; **11**, 528. Z. physik. Chem., **47**, 185.

before Stieglitz's paper appeared, and these chemists pointed out the bearing of their work on the hydrolysis of esters and cane sugar. Stieglitz, however, did not mention Bredig and Walton, or their priority in the proof of this fundamental point.

These chemists proved quantitatively that *iodide ions accelerate the velocity of the decomposition of hydrogen peroxide because an intermediate iodoso ion is formed*, as demanded by the mass law,

$$H_2O_2 + \bar{I} \rightarrow H_2O + \overline{IO},$$

(measurably slow reaction)

or

$$\frac{dC_{\tilde{o}}}{dt} = KC_IC_{H_2O_2},$$

and is decomposed by hydrogen peroxide as follows:

$$H_2O_2 + \overline{IO} \quad = \quad H_2O + O_2 + \bar{I}.$$

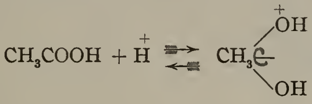
(immeasurably fast reaction)

After this quantitative use of the mass law in catalysis in the proof (to which Mr. Stieglitz does not refer) of the "point that the acceleration.....is, as a matter of experiment, due to salt and ion formation," Bredig and Walton made the following suggestions with reference to the catalysis of esters and cane sugar (p. 118, footnote): "The similarity of the catalysis of hydrogen peroxide by iodide ions to the inversion of sugar and the hydrolysis of esters by hydrogen ions leads to the idea that these catalytic reactions are also to be considered as consecutive reactions involving the addition and loss of the catalyzer (that is, the formation of hydrogen ion hydrates, according to Noyes, or of compounds from the cane sugar, or ester, and the acid, according to Baeyer and others)."

Bredig's quantitative work on the catalysis of hydrogen peroxide by iodide ions is as good evidence of the correctness of the views of Kastle, Euler, Acree, Bredig, Lapworth, Stieglitz, and Goldschmidt on the hydrolysis of esters, as was Mr. Stieglitz's work on imidoesters.

(5) Mr. Stieglitz's "point that the acceleration....is, as a matter of experiment, due to salt and ion formation" was also proposed by Lapworth and described in Mellor's "Statics and Dynamics" in 1904, although Stieglitz did not, in a public address on April 6, 1907, and in his recent note, give Lapworth credit for these ideas.

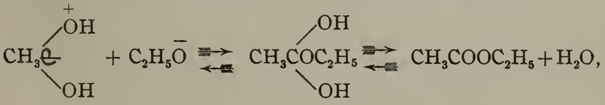
Mellor says (p. 289): "None of these expressions take account of the accelerating influence of hydrogen ions, and A. Lapworth, in consequence, has proposed a compromise between the ionic theory and the association hypothesis, namely, that 'the production of complex ions is at the bottom of a large number of organic reactions.' He suggests for the esterification of alcohol....



$$CH_3COOH + \overset{+}{H} \rightleftarrows CH_3C\begin{matrix}\overset{+}{O}H\\ OH\end{matrix}$$

see errata p. 823

a slow reaction, followed by the more rapid changes—



$$CH_3C\begin{matrix}\overset{+}{O}H\\ OH\end{matrix} + C_2H_5\bar{O} \rightleftarrows CH_3\overset{OH}{\underset{OH}{C}}OC_2H_5 \rightleftarrows CH_3COOC_2H_5 + H_2O,$$

which are in harmony with the observation that the velocity of hydrolysis of ethyl acetate is directly proportional to the concentration of the hydrogen ions."

(6) In 1906, and again in 1907, Heinrich Goldschmidt[1] proposed the idea that "it seemed possible to decide, by suitable combinations of catalyzing acid and the acid to be esterified, whether the intermediate reactions, which we are led to assume by the present views of catalysis, take place between the alcohol and the catalyzer or between the catalyzer and the acid which is to be esterified." But in at least one public address and in the note just published Mr. Stieglitz has overlooked Goldschmidt's ideas, which are practically the same as his own.

(7) We see then that Kastle, Euler, Acree, and Bredig all had priority over Mr. Stieglitz in every one of his funda-

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[1] Goldschmidt and Sunde: Ber. d. Chem. Ges., **39**, 711. Goldschmidt and Udby: Z. physik. Chem., **60**, 728.

mental ideas. Mr. Stieglitz put forward our ideas again as his own, without mentioning the name of any one of these four chemists, who had all "departed from the old idea" and "left the old beaten track." Mr. Stieglitz was informed several months ago by me that they have priority in these ideas, and that Acree and Johnson would give credit where it is deserved. Acree and Johnson gave full credit[1] in their article to all of the above colleagues, and to Stieglitz, in many places, and criticized some of the articles in the light of the most recent knowledge.

Mr. Stieglitz will get credit for his work on imidoester hydrolysis when he publishes it and shows us that he has proved that imidoester cations are hydrolyzed. His quantitative work will be a welcome and, I am sure, valuable addition to that of his colleagues.

(B) And now we come to the work in which Acree and Johnson claim priority over every one except Abel[2] and Euler,[3] whose work was published in German and reached America after the article by Acree and Johnson was in the hands of the editor. I did not claim priority,[4] as Stieglitz would have his readers believe, for *Kastle's idea of intermediate salt formation*, but I do share in the idea, and do claim priority, with Abel and Euler, for the view that the second and third laws of catalysis do not hold in some reactions. It was after very thoughtful consideration of the subject that we chose our experimental material and disproved the validity of the above two laws of catalysis.

Mr. Stieglitz not only presented as new the ideas already advanced by others, but, I take it from the *indirect* statement "there is not one single new principle presented in Acree's paper," that Mr. Stieglitz would now have his readers believe that *he* deserves credit for the discovery by Acree and Johnson that the second and third laws of catalysis do not hold in all reactions. Mr. Stieglitz does not face the issue squarely and state that he presented in the St. Louis report any ideas or experimental material that proved that the second and third laws do not hold in some reactions; his own words would be against him. I believe that if Mr. Stieglitz had at that time really had the very important idea that the second and third laws do not always hold, he would have been as eager then as he is now to get credit for the fact and would have said something about it in his St. Louis address. I quote Mr. Stieglitz concerning this second "so-called" law of catalysis, which postulates direct proportionality between the concentration of the catalyzer and the reaction velocity.

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[1] *Loc. cit.*, pp. 299, 300, 301, 335, 338, 339, 342, 345.

[2] Z. Elek. Chem., **13**, 555.

[3] Z. physiol. Chem., **52**, 146.

[4] See Acree and Johnson: THIS JOURNAL, **38**, 299, 300, 301, 335, 337, 338, 339, 341, 342.

Mr. Stieglitz states, in discussing the catalysis of esters, that (p. 745) "the simple application of our common laws of equilibrium to the proved fundamental idea of salt formation led, mathematically and chemically, *directly to the three principles mentioned above*."[1] Again, on p. 282 of the St. Louis paper: "We find that the velocity must in fact increase directly proportionate to the concentration of the hydrogen ions.....This consequence of our theory is evidently in perefect agreement with the well-known experimental results." On p. 283: "We find again that the change in the velocity of esterification demanded by the application of this theory is simply proportionate to the change in concentration of the hydrogen ions—which agrees with experience." Again, on p. 283: "The three important characteristic features of the catalysis—a velocity proportionate to the concentration of the hydrogen ions....all are in perfect agreement with this simple conception of the manner in which the catalyzer produces its apparently marvelous result."

Mr. Stieglitz did not intimate in *one* place in his article that he had any experimental material or ideas that would lead him to suspect that the second law of catalysis does not hold in all reactions. Acree and Johnson predicted theoretically and proved experimentally that the *second law of catalysis cannot hold in such cases as* (p. 349) *the hydrolysis*

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[1] Italics are mine.

of oximes and (p. 352) *the rearrangement of acylhalogenaminobenzene derivatives and other similar reactions.*

I quote Mr. Stieglitz's only words concerning the third "so-called" law of catalysis, which postulates that a change in the concentration of a catalyzer will not affect the equilibrium point of reversible reactions. Mr. Stieglitz says (p. 283, St. Louis report): "In other words the addition of the catalyzing acid will not affect the ultimate condition of equilibrium between ester, water, acid, and alcohol." Again, on p. 284: "the catalyzer apparently acting only by its presence and not changing the final condition of equilibrium."

I do not find anywhere in Mr. Stieglitz's article an intimation that he had any experimental material or ideas which would lead him to suspect that the third law of catalysis does not hold in all reactions. Acree and Johnson predicted theoretically and proved experimentally that the third law of catalysis cannot hold in such cases as (pp. 349, 351) with the oximes and, *in general*, (p. 351, 353) "in those reversible reactions in which the velocity of one reaction is accelerated in proportion to the m power of the concentration of the catalyzer while the velocity of the reverse reaction is accelerated in proportion to the n power of the concentration of the catalyzer."

I both told and wrote Mr. Stieglitz *in detail*, in a friendly way, in *April and May*, that our theoretical and experimental conclusions disproved the validity of the second and third laws of catalysis, and he will doubtless give us credit for this in THIS JOURNAL, in his forthcoming article, which was received by the editor on Sept. 13. After he knew my results he tried, in a letter to me, to make it appear that he had predicted the same in his St. Louis paper; I have quoted his real conclusions above. It should be pointed out that Abel, Euler, and Miller and Clark[1] have all recently come to our conclusions theoretically and experimentally.

Acree and Johnson, and Acree and Nirdlinger[2] discussed a number of reactions which are catalyzed in a positive or negative sense by *bases*, *acids*, and *salts*, and showed in which the *active molecules* are *anions*, *cations*, or *neutral molecules*. We greatly broadened, both mathematically and experimentally, the point of view presented before by Kastle, Euler, Acree, Bredig, Lapworth, *Stieglitz*, Goldschmidt, and others, giving in every case full credit to each worker.

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[1] J. Physic. Chem., **11**, 353.

[2] THIS JOURNAL, **38**, 489.

(C) The impression that might be left with the reader by Mr. Stieglitz's section (2) (p. 745) that I spent the summer of 1905 in Chicago "to get Stieglitz's methods" and "discussing freely and with my consent with my collaborators, whose work was already completed, the ideas and investigations carried on in our laboratory," is not in accordance with the facts. I worked on *tautomeric compounds*, and was then directing graduate students in Johns Hopkins University in this line of work. While there I invited Mr. Stieglitz to collaborate with me (on tautomerism, and *not* on catalysis) for our mutual benefit, as he had published a paper[1] on tautomeric compounds in which some wrong[2] ideas were advanced. We did not work together, nor did we converse one hour during the summer. *Absolutely* the only thing that I knew of Mr. Stieglitz's work was learned in perhaps a ten-minute talk with one of my former students (Schlesinger), who told me that he had shown that imidoester cations are hydrolyzed; for this fact Mr. Stieglitz was given ample credit[3] by Johnson and myself. I refreshed Mr. Stieglitz's memory on these matters in September, 1907, orally and later by letter.

On April 1, 1907, a week before Mr. Stieglitz's address at the Johns Hopkins University, an article by Acree and Johnson[4] appeared, in which they showed that the second and third laws of catalysis cannot hold in all reactions. Mr. Stieglitz was made aware of these results before his address.

In answer to Mr. Stieglitz's statement (note, p. 745) that the salts of esters and acids were treated by him "as oxonium bases, exactly as Acree has also now done," I must answer

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[1] J. Am. Chem. Soc., **25**, 1119.

[2] Acree: This Journal, **37**, 72.

[3] Acree and Johnson: This Journal, **38**, 299, 301, 335, 338, 339, 342.

[4] *Ibid.*, **37**, 410.

(1) that Mr. Stieglitz failed to mention in his St. Louis paper that Kastle,[1] Collie and Tickle, Baeyer and Villiger, Werner, Brühl, Archibald and McIntosh, Walden, van't Hoff, and a host of others had treated them as oxonium bases and salts long before, and (2) that Acree and Johnson, on p. 337, gave *four different structures* for these salts and said: "All four may be in tautomeric equilibrium."

JOHNS HOPKINS UNIVERSITY,
Dec. 13, 1907.

REVIEW.

GLEICHGEWICHTE DER STEREOMEREN. Von W. MEYERHOFFER, Weil. Prof. Dr. Mit einem Begleitwort von PROF. DR. J. H. VAN'T HOFF, und 28 Figuren im Text. Leipzig und Berlin: Druck und Verlag von B. G. Teubner. 1906. pp. 71.

A feeling of sadness comes over one on reading this little monograph. It is the last contribution to physical chemistry from that earnest and fruitful investigator, Meyerhoffer. Cut down at the height of his activity, he will ever be remembered by his colleagues and friends as a distinct loss to our science.

A paragraph from the preface by van't Hoff will show the attitude of this great leader towards his younger colleague.

"Die 1892 gleichzeitig deutsch und französisch erschienene Stereochemie war seine erste grössere zusammenfassende Arbeit; die jetzt 14 Jahre später, erschienene Veröffentlichung auf demselben Gebiet sollte die letzte sein. Sie berürht dasjenige in der Stereochemie, was allgemein auch den Nichtchemiker interessiert, nämlich die Frage, ob die optische Aktivität eine Lebensaüsserung ist, auf welchen Standpunkt sich bekanntlich Pasteur stellte. Die Entdeckung, dass die Trennung der entgegengesetzt aktiven Isomeren und damit die Ausscheidung derselben eine Temperaturfrage ist und mit einer bei bestimmter Temperatur eintretenden Umwandlungserscheinung zusammenhängt, brachte die Erscheinung in anderes Licht, und die vorliegende Arbeit gibt die Gesetze, welche diese Umwandlungserscheinung beherrschen. Dieselben bringen die Ausscheidung von optisch-aktiven Verbindungen in nahen Zusammenhang mit der Spaltung von Doppelsalzen."

The aim and result of the work recorded in this monograph is summarized in the above paragraph. H. C. J.

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[1] For references see Acree and Johnson: *Loc. cit.*, p. 298.

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SOME EFFECTS OF SUNLIGHT UPON COLORLESS GLASS.

BY ROSS AIKEN GORTNER.

Within recent years, a number of instances have been reported, from various parts of the world, concerning the violet coloration of glass when exposed to the sunlight.[1]

Fischer[2] has induced the same change in colorless glass, containing a comparatively small proportion of manganese, by exposure to the rays of a mercury lamp, thus showing that the change is due to the ultraviolet rays.

Up to the present time only one instance, which was observed by the writer,[3] has been reported indicating the time of exposure actually required to produce the change in the color of the glass.

On July 9, 1906, twenty-two specimens of glass were firmly fastened to a board by means of aluminium wire and the board exposed upon the slate roof of a building at Lincoln in a position facing the south and inclined at an angle of about 45°.

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[1] Crookes: Chem. News, **91**, 73 (1905). Avery: J. Am. Chem. Soc., **27**, 909 (1905). Simpson: Chem. News, **91**, 236 (1905). Rueger: J. Am. Chem. Soc., **27**, 1206 (1905). Alway and Gortner: THIS JOURNAL, **37**, 1 (1907).

[2] Ber. d. chem. Ges., **38**, 946 (1905).

[3] THIS JOURNAL, **37**, 1 (1907).

The spot selected was about 75 feet above the ground and was exposed to the direct rays of the sun for the entire day excepting, perhaps, in June and July for an hour before sunset when a low tower on the west cast a shadow on the board. The specimens, when on the building, were at an elevation of about 1200 feet above sea level.

Specimens 1 to 12, inclusive, were rectangular 4-ounce bottles of the same make and were obtained from a local dealer. They were exposed, filled with various substances, numbers 1 to 6 being filled with chalk colored, respectively, with picric acid, indigo, methyl violet, "wasserblau," malachite green, and sodium eosin. Number 7 was filled with manganese dioxide, number 8 with lampblack, number 9 with sodium eosin solution, number 10 with potassium permanganate crystals, number 11 with chalk, while number 12 was exposed empty. Numbers 7, 8, and 10 were filled with their respective contents in order to determine what truth there might be in the theory of Chas. Rueger[1] that glass might become "violet by lying for some time in the proximity of bodies heavily charged with manganese." Number 13 was a bottle of a different make and was exposed filled with potassium chromate crystals. Number 14 was the base of a broken goblet which was found upon the street and which, as yet, showed no trace of violet coloration although it might have been exposed to the sunlight for some time. Number 15 was a small glass funnel, number 16 a small round solution bottle, number 17 a 50 cc. Erlenmeyer flask of Jena glass, number 18 an ordinary round 50 cc. flask, number 19 a small homeopathic vial of American manufacture, number 20 a piece of hard glass tubing, and numbers 21 and 22 pieces of soft glass tubing. Numbers 15, 16, 17, 20, 21, and 22, were secured from the "Vereinigte Fabriken," Berlin.

One month after exposure the specimens were examined and it was found that numbers 13, 14, 21, and 22 had become slightly violet, number 13 being of so decided a violet tinge that the coloration was noticeable several feet away.

The specimens of glass then remained undisturbed until the 21st of March, 1907, when they were again examined. At that time they all showed some violet coloration excepting numbers 15, 16, 17, and 20, which still remained colorless. Numbers 13 and 21 had, by this time, become intensely violet. Number 22 could not be found, evidently having been blown away by the wind.

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[1] J. Am. Chem. Soc., **27**, 1206 (1905).

On May 31, 1907, the board was removed from the roof and the bottles, after being cleaned, were given a close inspection, with the following result: number 1 was distinctly violet on the upper face, less violet on the sides, but still enough so that the coloration was plainly visible, and almost colorless on the back. Numbers 2, 4, 5, 6, and 11 differed in no way from number 1. Number 3, which had contained chalk colored with methyl violet, was of a deeper color on the upper face and sides and was also of a faint violet on the back. Number 7 (filled with manganese dioxide) and number 8 (filled with lampblack) were indistinguishable from each other, being less violet on the surface and sides than the preceding numbers and showing almost no color on the back. Number 9 had been broken by the freezing of its contents; the violet tinge on the face and sides was pronounced, and on the back, less so. No 10, containing potassium permanganate crystals, was the least colored of the series 1–12, being slightly less violet than numbers 7 and 8. There was a faint violet tinge upon the upper face and almost no color whatever upon the sides and back. Number 12, being empty, was of a uniform violet throughout and the color could not be distinguished from that of the face of number 1. Number 13 was a very intense violet upon the face and sides and of a deep violet on the back. This is the best specimen of violet colored glass that I have been able to secure in Nebraska, although it is surpassed in intensity of coloration by some specimens from the steppes of Canada and from New Mexico.[1] Number 14 was of a deep violet throughout, being more intense in color than number 12 and much less intense than number 13. The shade was slightly deeper than on the back of number 13. Numbers 15, 16, 17, and 20 showed no trace of violet coloration. Numbers 15, 16, and 20, as will be shown later in the table of analyses, contained no manganese, and number 17, although

[1] The specimens from New Mexico were secured from Dr. Avery.

containing manganese, was not colored violet by the action of the sunlight. An explanation for this may be found in the composition of Jena glass which may prevent the necessary chemical change from taking place. Fischer[1] met with similar results when Jena glass was exposed to the rays from a mercury lamp. Numbers 18 and 19 were distinctly violet throughout. Number 21 was distinctly violet when seen from the side, even at a distance of several feet, and when viewed lengthwise, the violet coloration was very intense, being but a shade lighter than number 13.

In order to obtain the manganese content, the method of H. Noll[2] was employed. Portions of the specimens were ground to a powder, fused with sodium and potassium carbonates, dissolved in dilute hydrochloric acid, precipitated with ammonia and bromine water, and allowed to stand for 12 hours. The precipitate was then filtered out, washed, and treated with 1 gram potassium iodide and 4 cc. concentrated hydrochloric acid. After standing for five minutes the iodine set free was titrated with N/100 sodium thiosulphate. From the iodine set free the manganese is calculated.

The color of the beads which were obtained by the fusion ranged from a deep purple in number 13 to colorless in numbers 15, 16, and 20. The range of coloration was in the following order: 13, 11, 19, 18, 21, 14, and 17, 13 being the most colored and 17 the least. The beads obtained from numbers 1 to 12 were indistinguishable and therefore number 11 was selected to represent the series.

The accompanying table gives the percentage of manganese and shows the relation of this to the change in color on the face of the specimen. "Slight" means slightly violet, "pale" means pale violet, etc.

The influence of the exposure of glass is well illustrated by the color of the basement windows of a church near Lincoln which has been built for five years. The windows are of pressed glass, and on the south and west sides are of such a distinctly violet color as to be easily noticeable a hundred yards away,

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[1] Ber. d. chem. Ges., **38**, 946 (1905).

[2] Centrabl., 1907, 1 1223 (Apr. 17).

No. of sample.	Description of sample.	Per cent of manganese.	Color after 1 month.	Color after 8 months.	Color after 11 months.
15	small funnel (Verein. Fabrik.)	0.000	none	none	none
16	100 cc. bottle (Verein. Fabrik.)	0.000	"	"	"
20	hard glass tubing (Verein. Fabrik.)	0.000	"	"	"
14	base of goblet	0.049	slight	distinct	deep
17	50 cc. Erlenmeyer flask (Jena glass)	0.072	none	none	none
1	bottle with chalk colored with picric acid	0.075 to 0.087	"	light	distinct
2	" " " " " indigo		"	"	"
3	" " " " " methyl violet		"	distinct	" deeper than No. 1
4	" " " " " "wasserblau"		"	light	distinct
5	" " " " " malachite gr'n		"	"	"
6	" " " " " sodium eosin		"	"	"
7	" " manganese dioxide		"	pale	light
8	" " lampblack		"	"	"
9	" " sodium eosin solution		"	distinct (broken)	distinct
10	" " potassium permanganate crystals		"	faint	very light
11	" " chalk		"	distinct	distinct
12	" empty		"	"	"
19	homeopathic vial (American manufacture)	0.14	"	"	deep
18	round flask (American 50 cc.)	0.17	"	"	"
21	soft glass tubing	0.20	pale	"	"
13	bottled with potassium chromate crystals	0.34	distinct	deep	very deep
22	soft glass tubing	(?)	"	lost	lost

while on the north and east sides there is almost no coloration. When closely examined, the violet coloration is so intense as to be comparable only to the deeper-colored glass found on the high plains of Canada. The coloration is as deep as that of number 13 although the manganese content is only 0.126 per cent, the deep color being probably due to the length of exposure.

Beside the specimens of violet-colored glass secured in this vicinity, the writer has found many scattered over eastern and northern Nebraska and has received some from the second steppe of Canada. The latter came from southern Saskatchewan at an elevation of about 2000 feet.

Summary.

Glass containing a relatively large percentage of manganese may show a violet coloration when exposed to sunlight for a period of less than a month, the degree of coloration being proportional to the manganese content.

Exposure of less than a year will produce a violet coloration in most glasses containing only a small percentage of manganese, but this coloration will become more pronounced when the time of exposure is increased.

Should a glass be colored violet by the action of sunlight, proof is furnished that the glass contains manganese. However, not all glasses containing manganese are colored violet by exposure to sunlight, as is shown by the Jena Erlenmeyer.

A background or subsoil containing manganese or ores of manganese will have no influence upon the coloration of glass lying upon it.

A violet background is more favorable to the action of the ultraviolet rays than other colors: white, yellow, blue, and red act alike and seem to have no effect, while brown and black seem to have a retarding effect.

LINCOLN, NEBRASKA,
August 1, 1907.

STUDIES ON SOME SOILS FROM SASKATCHEWAN.

By Leverne L. Clark, Ross A. Gortner, and Carey E. Vail.

Hilgard[1] has pointed out that, while the fine soil particles (grains of a diameter of less than 0.025 mm.) under humid conditions contain almost the whole of the available plant food of the soil, it is different in regions of deficient rainfall. In the latter "much actual plant food may be present in rather coarse sandy soils, almost devoid of clay; such as in humid climates would be likely to be found wholly barren."[2] This is well illustrated by the work of Loughridge[3] on a generalized soil of the state of Mississippi and also on sandy and adobe soils of California. Later investigations by Rudzinski[4] and by Mazurenko[5] on loess and podzol soils from European Russia corroborate the work of Loughridge.

The analyses reported in this article are those of a boulder clay from southern Saskatchewan.[6] All of the samples are from the region of treeless plains, characterized by a low rainfall which occurs almost exclusively during the growing season. Seepage on the heavier soils probably does not occur to any appreciable extent. The mechanical analysis of a sample of boulder clay was made with the following results:

	Per cent.
Gravel, 2.0 to 1.00 mm.	1.7
Coarse sand, 1.0 to 0.5 mm.	5.2
Medium sand, 0.5 to 0.25 mm.	5.6
Fine sand, 0.25 to 0.10 mm.	14.1
Very fine sand, 0.10 to 0.05 mm.	12.3
Coarse silt, 0.05 to 0.016 mm.	16.2
Fine silt, 0.016 to 0.005 mm.	19.5
Clay, 0.005 to ?	26.1
Total	100.7

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[1] Hilgard: Soils, pp. 87 and 386.

[2] *Ibid.*, p. 88.

[3] Report, Agr. Exp. Sta., Univ. of Cal., 1898–1901, Part 1, p. 33.

[4] Exp. Sta. Record, **16**, 345 (1904–05). Izv. Moscow Selsk. Khoz. Inst. (Ann. Inst. Agron. Moscow), **9** (1903), No. 2, pp. 172–234, pls. 5.

[5] Exp. Sta. Record, **16**, 344 (1904–05). Inaug. Diss., Munich; abs. in Zhur. Opuitn. Agron. Jour. Expt. Landw., **5** (1904), 1, pp. 73–75.

[6] Alway: This Journal, **36**, 580 (1906). Alway and McDole: *Ibid.*, **37**, 275 (1907).

The Vertical Distribution of Soluble Salts in the Soil.

A known weight of air-dried soil of each foot section was treated with a known volume of distilled water and allowed to stand with frequent shaking for 72 hours. The soil was then allowed to settle and the supernatant liquid siphoned off and filtered through double "barium" filters. An aliquot portion was then evaporated to dryness on a water bath in a platinum dish and dried to constant weight at 100°. The following were the percentages of soluble salts found in five different bores.

No. of bore.	1.	2.	3.	4.	5.
1st foot	.40	.27	.16	.28	.26
2nd foot	.26	missing	.12	.22	.15
3d foot	.15	.15	.11	.12	.05
4th foot	.07	.10	.10	.09	.06
5th foot	.05	.08	.06	.08	.04
6th foot	.06	.09	.07	.19	.05
Average	.16	.14	.10	.17	.10

The Composition of the Water-Soluble Portion of the Soil.

Equal quantities of each foot section of air-dried soil were mixed and treated with a known volume of water. After standing, with frequent stirring, for 72 hours, the supernatant liquid was siphoned off and filtered. A portion was evaporated to dryness in a platinum dish and dried to constant weight at 100° in order to ascertain the total alkali present. The remainder was analyzed with the following results:

	Per cent.
Na	14.18
K	1.75
Mg	11.04
Ca	2.79
SO_4	47.45
Cl	10.84
CO_3	3.42
H_2O (by difference)	7.53
Total	100.00

Chemical Composition of the Soil Particles of the Different Sizes.

The beaker method of separation was used, the soil being first boiled with distilled water until it was in a fine state of division, each grain being separate from the others. Equal portions of each foot section were mixed and, after boiling, separated by means of decantations from beakers into the various-sized grains. The clay which remained suspended in the water was precipitated by means of ammonium chloride, the clear liquid siphoned off, and the precipitated clay dried and powdered. The high percentage of volatile matter found in the clay is due partly to the presence of ammonium chloride. Particles of from 1.0 to 0.05 mm. in diameter are classified as sand, from 0.05 to 0.016 mm. as coarse silt, from 0.016 to 0.05 mm. as fine silt, and smaller than 0.005 mm. as clay.

Hilgard's method[1] was used in the chemical analysis of the separated portions. The following results were obtained from the four portions into which the soil was separated:

	Sand.		Coarse silt.		Fine silt.		Clay.	
Insoluble matter	82.85	85.03	59.05	64.86	31.95	53.63	15.24	43.51
Soluble silica	2.18		5.81		21.68		28.27	
CaO		4.93		10.29		9.36		0.84
FeO_3		1.54		2.19		5.74		8.59
Al_2O_3		0.60		1.74		7.50		11.87
Mn_2O_7		0.07		0.25		0.14		0.16
MgO		1.40		4.79		3.57		2.23
Na_2O		0.14		1.04		.82		1.12
K_2O		0.11		.58		1.52		2.08
CO_2		4.59		12.42		8.87		0.29
SO_3		0.06		0.15		0.07		0.07
P_2O_5		0.10		0.22		0.22		0.30
Volatile matter		0.37		2.76		7.83		28.63
Total		98.94		101.29		99.27		99.69

LINCOLN, NEBRASKA,
August 10, 1907.

[1] Circular No. 6, Agricultural Exp. Station, University of California.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

STUDIES IN CATALYSIS. II. THE CATALYSIS OF IMIDOESTERS.

By Julius Stieglitz.

In the first paper,[1] it was stated that an imidoester is decomposed by water in two ways,

$$RC(:NH)OR' + H_2O \rightleftarrows RCOOR' + NH_3 \qquad (1),$$

and

$$RC(:NH)OR' \rightleftarrows RC \vdots N + HOR' \qquad (2).$$

The first action, which can just be detected and measured in aqueous solutions,[2] is accelerated enormously by the addition of acids, and it was shown in the first report that the acceleration is proportionate to the salt formed. Since dilute solutions, in which the imidoester salts are very largely ionized, were used, the conclusion was drawn that the reacting component for expression (1) is really the positive imidoester ion, which is decomposed by water thus:

$$RC(:\overset{+}{N}H_2)OR' + HOH \rightleftarrows RCOOR' + \overset{+}{N}H_4 \qquad (3).$$

This conclusion is borne out by Schlesinger's determinations[3] of velocities with more concentrated solutions of the imidoester salts, for which the degrees of ionization were also determined. These results will be briefly discussed below in Part VIII.

The second of the above reactions is accelerated enormously by the addition of alkalis. This fact is particularly interesting, as it draws still closer the parallelism between ordinary esters and the imidoesters. According to our theory of catalysis, the acceleration by the alkalis or, rather, their hydroxyl ions, would be due, by analogy to the action of acids, to salt formation between the alkalis and the imidoesters, from which the possession of weak acid properties and, consequently, of an amphoteric character must follow. The application of our theory to this case will be considered below in Part VI.

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[1] This Journal, **39**, 29 (1908).

[2] *Vide* a later paper by Miss Barnard.

[3] *Vide* a later paper by H. I. Schlesinger.

The reacting component, then, for expression (2) is again not the imidoester itself, but rather its negative ion, the velocities having been found proportionate to the concentration of this ion. We have

$$\mathrm{RC}(:\overline{\mathrm{N}})\mathrm{OR}' \longrightarrow \mathrm{RC} \vdots \mathrm{N} + \overline{\mathrm{O}}\mathrm{R} \qquad (4).$$

Besides these two reactions, we have still a third one, the study of which has been particularly interesting: in purely aqueous solutions, when neither acid nor added alkali is present, we also have a decomposition of the imidoester into nitrile and alcohol according to expression (2), and the reacting component in this case is the *nonionized* or molecular imidoester. This action is very much slower than either of the ion reactions under the influence of acids or bases. This possibility was considered and examined carefully: whether the imidoester being a base and rendering the solution distinctly alkaline, the decomposition in aqueous solution might not represent a case of autocatalysis, proceeding really according to expression (4) under the influence of its own hydroxyl ions, rather than a third reaction of the imidoesters. But from a rigorous analysis of the case, the conclusion must be drawn that the velocity in aqueous solution is chiefly due to a slow decomposition of the nonionized substance according to (2), the velocity being found much greater than could be accounted for by the amphoteric properties of the imidoesters. The action will be discussed in detail in Part VII.

As giving an insight into the nature of the reactions of organic compounds (and the same considerations apply equally to inorganic compounds), it is considered extremely interesting to have thus found that the imidoesters react by means of three components, each reacting with characteristic velocity constants: their positive ions forming, with water, acid esters and ammonium ions; their negative ions forming nitriles; and the nonionized molecules forming nitriles and alcohols also, but with their own characteristic velocity constant. It is particularly noteworthy that the reaction velocities of the ion forms are very much greater than those of the non-ionized molecules.

Schlesinger's determinations of the velocities of decomposition of the imidoester salts in more concentrated solutions led to the recognition of a *salt effect* or *salt catalysis*, influencing the velocity of decomposition of the imidoesters by water, just as there is a salt catalysis of ordinary esters, cane sugar, etc. Similar effects were then recognized in experiments carried out with Derby[1] and McCracken[2] on the speeds of reaction of imidoesters in the presence of an added excess of hydrochloric acid. Rough determinations of the order of this salt acceleration have been made and have suggested a very interesting conclusion, but as a very thorough investigation of this part of the problem has been made by Miss Barnard,[3] giving a better foundation for our conclusions, a brief discussion of our earlier results in Part VIII will be sufficient.

In the first paper attention was called to the conclusion that there is a tendency, under the influence of acids, toward a decomposition resulting in the formation of the ion of a stronger base from the positive ion of a weaker base—the ions of the imidoesters, for instance, the weaker bases, forming ammonium ions, the ions of a much stronger base. An investigation of the question whether the reaction velocities are greater, the greater the difference in the affinity constants of the two bases, was carried out by Mr. McCracken and will be discussed in Part IX.

In this tendency, studied experimentally and quantitatively for the imidoesters, we have still another analogy between the imidoesters and ordinary esters,[4] and as the substitution of imidoesters, for which we have been able to determine experimentally all the constants and factors involved in our calculations, for ordinary esters in the experimental study of the theory of catalysis forms a vital step in our study, the parallelism between the two classes of esters, as it now appears as the results of our work, will be summarized in Part X.[1]

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[1] *Vide* a later paper by Ira Derby.

[2] *Vide* a later paper by W. McCracken.

[3] *Loc. cit.*

[4] Euler: Z. physik. Chem., **36**, 419 (1901).

VI.[2] The Catalysis of Imidoesters in Alkaline Solutions.

That imidoesters, $RC(:NH)OR'$, should have weak acid properties, besides being pronounced bases, is not surprising in view of the fact that the very much stronger, closely related bases, the amidines, have the power to form salts with metals, as has been known for some time. Thus, phenylmethylisourea, $C_6H_5NHC(:NH)OCH_3$, which is at the same time an amidine and an imidoester, forms a silver salt, $(C_6H_5)NHC(:NAg)OCH_3$.[3] Carbamide itself, as is well known, forms a disilver salt, to which the structure $NH_2C(:NAg)OAg$ must be assigned. The substitution of a negative group, such as C_6H_5, $NO_2C_6H_4$, for the positive amide group, NH_2, must strengthen the acid tendencies of the molecule, although it still remains an exceedingly weak acid, as is hydrocyanic acid, $C:NH$,[4] which may be considered the prototype of all these acids.

For an exceedingly weak acid,

$$RC(:NH)OR' \rightleftarrows RC(:\overset{-}{N})OR' + \overset{+}{H} \qquad (4),$$

for which we have,

$$C_{neg.ion} \times C_H = k_{aff.} \times C_{mol.} \qquad (5).$$

We may put the molecular concentration equal to the total concentration of the ester, the ionized part being negligible in calculating $C_{mol.}$, and taking the ionization of water into account, we have

$$C_{neg.ion} = k_{aff.} \times \frac{C_{ester}}{C_H} \qquad (6),$$

$$= \frac{k_{aff.}}{k_{HOH}} \times C_{ester} \times C_{OH} \qquad (7).$$

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[1] Later papers will take up in detail the question of the catalytic actions of the imido- and ureaesters with ammonia and ammonium chloride, and the question of the "salt effect". The investigations, carried out by Miss Edith Barnard, Miss Katharine Blunt, and Mr. R. A. Hall, have already been completed.

[2] Parts I. to V. are in the first report, THIS JOURNAL, **39**, 29 (1908).

[3] Stieglitz and Bruce: J. Am. Chem. Soc., **26**, 435 (1904).

[4] $K_{HCN} = 1.3 \times 10^{-9}$. Ammonia unquestionably ionizes to a very slight degree into $\overset{+}{H}$ and $\overset{-}{NH_2}$; the metal amides are derived from the $\overset{-}{NH_2}$ ions and the reactions of ammonia in which it is absorbed must be due to these ions.

For a reaction

$$\mathrm{RC(:\bar{N})OR'} \rightarrow \mathrm{RCN} + \mathrm{\bar{O}R'} \qquad (2),$$

in which the negative ion is the reacting component, we have[1]

$$\frac{dx}{dt} = k_v \times C_{neg.ion} \qquad (8).$$

By substituting into equation (8) the value found for $C_{neg.ion}$ in equation (7), we obtain

$$\frac{dx}{dt} = k_v \times \frac{k_{aff.}}{k_{HOH}} \times C_{ester} \times C_{\dot{O}H}$$

$$= K_v \times C_{ester} \times C_{OH} \qquad (9).$$

For an exceedingly weak acid then, whose negative ions are decomposing according to (2), we should find the velocity of the decomposition proportionate to the total concentration of the ester and to the concentration of the hydroxyl ion.[2]

Dr. Schlesinger, using this equation, obtained excellent constants for five imidoesters (methyl, ethyl, propyl, isopropyl imidobenzoate and methyl imido-*m*-nitrobenzoate). Even for the most stable (slowest reacting) imidoester, isopropyl imidobenzoate, the velocity constant was a very high one, $K_v = 0.265$ at 25°, and for the nitro ester the constant was 3.66. These constants are very much larger than those for the velocities of decomposition in acid solutions (see the first report). And so the imidoesters resemble the esters also in being decomposed much more rapidly by alkalis than by acids.

VII. *The Decomposition of Imidoesters in Aqueous Solutions.*

The decomposition of an imidoester in aqueous solution into an alcohol and a nitrile (expression 2) may be the result of three different causes:

(1) The substance actually undergoing the decomposition might be the nonionized base. As the imidoesters are ex-

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[1] $C_{neg.ion}$ is a function of x.

[2] Equations (8) and (9) are the fundamental equations for reactions—so-called catalytic—accelerated by alkalis. They correspond to the equations given in Vol. IV, p. 281, Congress of Arts and Science, St. Louis, 1904, and in the first paper [THIS JOURNAL, **39**, 29 (1908)] for reactions accelerated by acids.

ceedingly weak bases and are hardly ionized at all, the reaction velocity must then be proportionate to the total concentration of the esters, and we have a reaction of the first order,

$$\frac{dx}{dt} = K_{mol.} \times (C - x) \qquad (10),^1$$

and

$$K_{mol.} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (11).$$

As is shown in the tables given below, excellent constants are obtained when the reaction velocities are calculated according to this equation.[2]

(2) The reacting component may be the negative ion of the imidoester. Schlesinger having found that hydroxyl ions accelerate the decomposition into nitrile and alcohol, and these being the chief products of decomposition also in aqueous solution, it could very well be that in the aqueous solution *the hydroxyl ions of the base itself* cause the decomposition by the formation of more negative imidoester ions—by a kind of autocatalysis.

For this action we have the velocity of the reaction given by the equation

$$\frac{dx}{dt} = K_{neg.ion} \times C_{ester} \times C_{OH} \qquad (9).^3$$

If the decomposition of the imidoester by water is primarily due to the negative ions and the hydroxyl ions, as expressed in this equation, then, the imidoesters being weak bases and at the same time weak acids (amphoteric), the concentration of the hydroxyl ions would be a variable dependent at every moment on the concentration of the free base. If salt formation occurs to any but a negligible extent, the concentration of the hydroxyl ions formed from the base would be very largely affected by the increased concentration of the positive

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[1] $C - x$ represents the concentration of the ester at any moment t.

[2] From what follows, it will become apparent that the mere fact that a very good constant was obtained according to (10) and (11) would not warrant one in proceeding no further in the analysis of the action—a second equally good constant might appear by another interpretation (see below).

[3] *Vide VI.*

ions as a result of salt formation. The ionization constant of the ester as an acid is so small that we have not yet attempted to determine it and we have deemed it sufficient to consider the two extreme possibilities of the case. The first —the imidoesters being such strong bases that their solutions react decidedly alkaline—is that the acid character may be considered so weak as not to affect the value of the hydroxyl concentration by the production of a salt and its positive ions. This assumption leads to a *maximum* possible value for the concentration of hydroxyl ions and this restriction is quite sufficient for the purpose of this discussion. The second extreme assumption is that the positive and negative ions are formed *chiefly from the salt* produced by the amphoteric character of the esters. Under (2A) the first extreme assumption will be treated, under (2B) the second one.

(2A) For a weak base we have

$$C_{pos.ion} \times C_{OH} = k_{aff.} \times C_{mol.} \qquad (12),$$

and if salt formation can be neglected,

$$C_{pos.ion} = C_{OH} \qquad (13).$$

We may also put, as a very close approximation,

$$C_{mol.} = C_{ester} \qquad (14).$$

Then, from (12), (13), and (14), we have at any moment,

$$C_{OH} = \sqrt{k_{aff.} \times (C—x)} \qquad (15),$$

in which (C—x) represents the concentration of the imidoester at any moment. C_{OH} will represent, then, a *maximum* concentration of hydroxyl ions, according to the assumption made.

Substituting the values for C_{OH} and for C_{ester} in equation (9), representing the velocity of the reaction, we have

$$\frac{dx}{dt} = K_{neg.ion} \times \sqrt{k_{aff.} \times (C—x)} \times (C—x) \qquad (16),$$

and

$$t = \frac{1}{K_{neg.iou.} \sqrt{k_{aff.}}} \int \frac{dx}{(C—x) \times \sqrt{C—x}} \qquad (17).$$

Integrating, we find

$$K_{neg.ion} = \frac{2}{t \times \sqrt{k_{aff.}}} \left(\sqrt{\frac{1}{C - x_t}} - \sqrt{\frac{1}{C}} \right) \qquad (18).$$

Or, if we express the concentrations in terms of parts of 1 gram molecule of ester in V liters,[1] and if v_0 and v_t cc. standard acid are used to neutralize a given volume of solution at the moments $t = 0$ and $t = t$, we have simply

$$K_{neg.ion} = \frac{2}{t}\sqrt{\frac{V}{k_{aff.}}}\left[\sqrt{\frac{v_0}{v_t}} - 1\right].$$

While fairly good constants were obtained according to this equation for single experiments, the values obtained with different concentrations of the base did not agree with each other. At the same time, the values thus calculated for $K_{neg.ion}$ are *very much higher* than the same constant as determined rigorously for the decomposition of the imidoesters in alkaline solutions.[2] For instance, for methyl imidobenzoate, catalyzed in the presence of barium hydroxide, $K_{neg.ion}$ is found by Schlesinger to be 1.97, but, as shown in the tables given below, if the reaction were an autocatalytic effect of the hydroxyl ion of the imidoester, in aqueous solution the constant would range between 20 and 40. The determinations for the other imidoesters show similar differences.

In other words, the velocity of decomposition in aqueous solutions is far too great to be accounted for by the decomposition of the negative ion by a process of autocatalysis, analogous to the catalysis by alkalis as discussed in Part VI., although we have assumed a maximum possible concentration of the hydroxyl ion. Consequently this interpretation of the action must be rejected.

(2B) On the basis of the second extreme assumption for the condition of an imidoester in aqueous solution, *viz.*, that its ionization is chiefly due to its amphoteric character and the ionization of the salt obtained from the acid and the basic forms, we have, according to Arrhenius, just as for aniline acetate,

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[1] $C = 1/V$.

[2] Page 169.

$$\frac{C_{neg.ion} \times C_{pos.ion}}{C^2_{ester}} = \frac{k_{acid} \times k_{base}}{k_{HOH}} = K \qquad (20).^1$$

In accordance with the assumption made that the ions are derived chiefly from the salt, we may put

$$C_{neg.ion} = C_{pos.ion},$$

and have then

$$\frac{C^2_{neg.ion}}{C^2_{ester}} = K,$$

or

$$C_{neg.ion} = \sqrt{K} \times C_{ester} = K' \times C_{ester} \qquad (21).$$

In other words, for an amphoteric substance, such as this, if the reaction velocity is found proportionate to the total nonionized substance, C_{ester}, as expressed in equation (10) and as is actually found by experiment (see below), a constant would also result by putting the reaction velocity proportionate to the concentration of the negative ions (or the positive ions) as the reacting substance, since, according to (21), the concentration of the ions is proportionate to that of the molecular substance (C_{ester}).

To decide between the two possibilities, with each of which the experimental data for purely aqueous solutions, considered alone, would agree, one need only compare the velocity constant for the negative ions of the amphoteric substance as found in aqueous solution with that found in solutions containing a known amount of alkali (hydroxyl ions). As was explained above, the speed of decomposition in aqueous solution is far too great to be accounted for by salt formation of the amphoter, even when the maximum value for C_{OH} and, consequently, the *maximum* value for the negative ions is assumed.[2] Consequently, although a *constant* would be obtained on the basis of this second extreme assumption (2B), that the ions come chiefly from the salt formation between the acid and the basic parts, it would agree even less with the other facts determined for the decomposition than did the as-

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[1] The amount ionized is considered negligible.

[2] $C_{neg.ions} = C_{ester} \times C_{OH} \times k.$ (7).

sumption made in (2A), and it must be rejected as not representing the main reaction under investigation.[1]

(3) The third theoretical possibility is that the reacting component in the decomposition of an imidoester in purely aqueous solution is neither the nonionized molecule nor its negative ion, but rather the positive ion of the amphoter. This possibility can be disposed of at once by the fact that the decomposition products of the positive ions in the presence of water have been shown to be an ester and ammonium ions; in the case under discussion, the chief products are the nitrile and an alcohol, and only traces of ester and ammonia are formed. The decomposition velocity cannot be due to the positive ion.

In the following tables two or three illustrative results are presented. The time is given in minutes in the first column. In the second column the volume of N/10 acid used to neutralize a given volume w of the base solution at any moment t is given. Column three gives the velocity constant calculated according to equation (11), the velocity being put proportionate to the total molecular concentration of the imidoester; and in the last column we have the constant calculated according to equation (19) as a reaction of the negative ions, accelerated autocatalytically by the alkaline properties of the imidoesters.

Table I.[2]*—Methyl Imidobenzoate at 25°.*

N/20. w = 25 cc.

t.	v_t.	4343 $K_{mol.}$	$K_{neg.ion.}$
0	12.49	....	....
60	12.27	1.28	19.6
200	11.85	1.15	16.8
260	11.70	1.09	....
400	11.28	1.11	16.7
1340	8.66	1.19	19.0
2750	5.72	1.23	22.0
4200	3.75	1.24	24.9

Mean: $K_{mol.} \doteq 0.00027$; $K_{neg.ion} = 19.8$

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[1] *Vide* Dr. Schlesinger's article for a second mathematical demonstration leading to the same conclusion.

[2] The data given in Tables I. and III. were obtained with Mr. Derby, and those in Table II. with Mr. Schlesinger.

Table II.—Methyl Imidobenzoate at 25°.

N/83.3. $w = 25$ cc.

t.	v_t.	$4343\ K_{mol.}$	$K_{neg.ion.}$
0	3.00	....	....
122	2.90	12.0	36.0
464	2.54	15.5	48.7
1489	2.00	12.0	39.3
1926	1.80	11.5	39.3
3191	1.34	10.1	40.4
4260	1.00	11.2	44.7

Mean: $K_{mol.} = 0.00026$; $K_{neg.ion} = 40.7$

Table III.—Ethyl Imidobenzoate at 25°.

N/40. $w = 25$ cc.

t.	v_t.	$4343\ K_{mol.}$	$K_{neg.ion.}$
0	6.19	1.18	16.82
350	5.63	1.18	16.82
1110	4.57	1.19	17.88
1580	4.01	1.19	18.60
2480	3.04	1.24	20.86
3220	2.43	1.26	22.44
3940	1.98	1.25	....
5380	1.38	1.21	25.26
6800	0.96	1.19	....

Mean: $K_{mol.} = 0.00028$; $K_{neg.ion} = 20.3$.

A consideration of these tables bears out the discussion given under (1) and (2): the values for $K_{neg.ion}$ are different for different concentrations of the base, as given in Tables I. and II., and they are much larger than the real values of the constants, as determined by Schlesinger in alkaline solution; the true value of $K_{neg.ion}$ for the methyl ester is 1.97, and for the ethyl ester it is 0.69.

On the other hand, in every case good constants, $K_{mol.}$, are obtained if the reacting mass of the substance decomposing into nitrile and alcohol be referred to the nonionized imidoester present, even for a time interval of 100 hours. The reaction velocities for such a decomposition are very small, very much smaller than the constants obtained for the decomposition of the negative ion into the same products, a nitrile and an alcohol; for the methyl ester, for instance, the decomposition constant of the molecules is only 1/7000 as large as the decomposition constant of its negative ion.

VIII. *The Salt Effect.*[1]

The acceleration by acids of the decomposition of imidoesters into acid esters and ammonia having been found proportionate to the salt formed by the acid with the imidoester, and the salts of imidoesters being very largely ionized in the dilute solutions used, it was thought probable that the reacting component was not all the imidoester salt but only the ionized part, *i. e.*, its positive ion.[2] In order to test this view Schlesinger has determined the velocities of decomposition for the hydrochlorides of methyl and ethyl imidobenzoate in solutions ranging from 0.05 to 0.5 molar at 25°, and has determined the degrees of ionization of these salts by conductivity methods. As was expected, the velocity constants, calculated for the total salt, showed a decided falling off with the increase of concentration and the consequent decrease of the degree of ionization; for the methyl ester, the constant fell from 0.00557 in 0.05 molar solution to 0.00477 in 0.5 molar solution, and for the ethyl ester from 0.00313 to 0.00246 for the same change in concentration. If the velocity constant referred to the total salt is called K_{salt} and α is the degree of ionization of the salt in the solution in question, then the velocity constant K_{ion}, referred to the ion concentration, as expressed in the fundamental equation of this theory of catalysis,

$$\frac{dx}{dt} = K_{ion} \times C_{pos.ion} \times C_H \times C_{OH} \qquad (22),^3$$

is

$$K_{ion} = \frac{K_{salt}}{\alpha} \qquad (23).$$

If there were no other accelerating or retarding force involved when the decomposition occurs in solutions of different concentrations, then K_{salt}/α should be a constant for the whole series of determinations. As a matter of fact, the values for K_{salt}/α in the determinations made with methyl and ethyl imidobenzoate formed a rapidly rising series as the solutions became more concentrated. This led to the suspicion that a second accelerating force is involved in the catalysis and it being well known that the catalysis of methyl acetate, cane sugar, etc., is subject to a decided acceleration by the presence of electrolytes,[1] a similar "salt effect" was suspected in the parallel case of the catalysis of these imidoesters. The imidoester salt itself, as an electrolyte, could have this effect in its own catalysis. The decomposition of a substance like cane sugar is accelerated from 100 to 150 per cent by a gram equivalent of ionized electrolyte, according to preliminary calculations made with Arrhenius' data, and so decidedly rising values for K_{salt}/α cease to be surprising.

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[1] This is a preliminary statement on the subject.

[2] See also the development for the catalysis of methyl acetate, Vol. *IV*, 281, Congress of Arts and Science, St. Louis (1904); THIS JOURNAL, **39**, 29 (1908); and the papers by Dr. Blunt and Dr. Hall.

[3] $C_{pos.ion}$ is a function of x.

One of the chief criteria of such salt effects is that, except for extremely dilute solutions, the acceleration produced is proportionate to the concentration of the electrolyte or, better, is proportionate to the concentration of the ionized portion of the electrolyte which is present. Considering the results for K_{salt}/α from this point of view, we soon found that the values showed, in fact, an acceleration of the action directly proportionate to the concentration of the electrolyte, *i. e.*, to the ionized portion of the imidoester salts themselves.

By plotting the values for K_{salt}/α and the concentrations of the ionized part of the salt, C_{ion} (the concentration of the positive or the negative ion present), on coördinates, a rectilinear curve is obtained and the velocity constant K_o for the imidoester ion alone, without any salt acceleration, can then be found by prolonging the curve to a point corresponding to a value for $C_{ion} = 0$. This value K_o having been found, the effect of the salt acceleration can be simply expressed in

$$K_{ion\ (theor.)} = K_o\,(1 + \beta\, C_{ion}) \qquad (24),$$

in which β is the acceleration produced by 1 gram equivalent ionized salt per liter, and C_{ion} is the concentration of the ionized part of the salt present. The equation represents an acceleration proportionate to the ion concentration and $K_{ion\ (theor.)}$ should agree with the experimental value $K_{ion\ (found)}$ or K_{salt} / α.

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[1] Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889). Euler: *Ibid.*, **32**, 348 (1900), etc.

The acceleration β is about 100 per cent per gram equivalent ionized salt for the hydrochloride of the methyl ester, *i. e.*, about of the same order as found for the salt effect on other catalytic actions. For the ethyl ester, it was found to be smaller, but the results with the methyl ester are considered the more reliable.

For a quantitative study of this salt effect thus discovered, very exact determinations of the degrees of ionization of the imidoester salts are of particular importance; they must be more exact than the determinations originally made by the ordinary methods in vogue could be considered to be. And so a careful investigation of this part of the subject was undertaken by Dr. Barnard; the effects of various added salts—potassium, sodium, and lithium chloride—were studied in mixtures prepared on the basis of the principle of isohydric solutions and the determinations of the degrees of ionization were checked by conductivity determinations of mixtures also prepared according to the principle referred to. A more detailed discussion of the salt effect, as studied for the imidoesters, is therefore postponed to a later paper based on Miss Barnard's results; but before closing this preliminary statement on the subject, I wish to call attention to the following: Salt catalysis, according to the most critical views on the subject, is supposed to consist, either wholly or partly, in an effect on the ionization of water, which, according to equation (22), is one of the active substances in the decomposition of the imidoesters, as it is in the catalysis of esters and of cane sugar; at the same time, it is supposed to effect possibly, also, the active mass of the substance undergoing decomposition.[1] It is an important question to determine experimentally whether the water really is affected. Now, for the imidoesters the concentration of the imidoester ion in equation (22) can be determined reliably by experiment with the aid of the isohydric principle, which Miss Barnard has proved may be successfully applied to mixtures of imidoester salts with other salts. If, then, the salt effect is in truth wholly due to a change of the ionization of water (forming the other active masses in equation (22)), then the acceleration factor β (equation 24) for a gram equivalent ionized salt, such as potassium chloride, ought to be the same for the different imidoester salts at a given temperature, irrespective of the actual value of the velocity constant K_o, *i. e.*, for a slow or a fast reacting imidoester.

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[1] Arrhenius: *Loc. cit.* Euler: *Loc. cit.*

With the consideration of this object in mind, the results obtained with Derby and McCracken[1] on the velocity of decomposition of methyl and ethyl imidobenzoates and of ethyl imido-*m*-nitrobenzoate—the latter reacts about ten times as fast as the former—as determined in the presence of an added excess of hydrochloric acid (up to 0.5 moles) were analyzed; the degrees of ionization of the imidoester salt and of the acid were estimated on the basis of the isohydric principle and β was calculated from the values for K_{salt}/α obtained. In both cases a good agreement with the requirements of equation (24) was found, and β was found to have the same value for the two esters which have such different velocity constants. For methyl imidobenzoate β was found to be 109 per cent; for the ethyl ester, 107 per cent; and for the ester of nitrobenzoic acid, 110 per cent.[2]

IX. The Velocities of Decomposition of the Imidoester Ions and the Affinity Constants of the Imidoesters.

The decomposition of an imidoester according to

$$RC(:\overset{+}{N}H_2)OR' + HOH \longrightarrow RCOOR + \overset{+}{N}H_4 \qquad (25)$$

represents the formation of an ion, NH_4, of a stronger base, ammonium hydroxide, from the positive ion of a weaker base, the imidoester. A general tendency of actions to take place in this direction in the presence of acids having been observed, and being, indeed, noticeable in all fields of chemistry, it was thought desirable to determine whether the difference between the affinity constant of the imidoester and that of ammonia affected also the speed of the above decomposition. Dr. McCracken[1] has found that the salts of the imidoesters which are the weakest bases are also decomposed most rapidly—in other words, the weaker the base from which the positive ion is derived, the greater the speed with which the latter is changed into the ion of the stronger base. For instance, for 25° we have:

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[1] See their papers in later numbers of THIS JOURNAL.

[2] Dr. Barnard's more exact determinations of the degrees of ionization of the imidoester salts modify the numerical values of these factors very much, but relatively in the same way. Our more rigorous experimental test of the above question answers it, more reliably, in the same sense.

Ester.	$10^5 K_{ion.}$	$10^{-9} k_{aff.}$
Ethyl imido-*m*-nitrobenzoate	3200	1.1
Methyl imidobenzoate	577	4.8
Ethyl imidobenzoate	377	11.0
Isobutyl imidobenzoate	350	12.5
Isoamyl imidobenzoate	349	16.8
Ethyl imido-β-naphtoate	251	7.9
Ethyl imido-*p*-toluylate	175	19.7

With the exception of the naphtoate, it appears, then, that the order of the affinity constants represents also the order of arrangement for the velocity constants, the latter decreasing when the former grow larger.

Euler[2] has arrived at the same conclusion for the velocity constants for the catalysis of the acid esters by making the not unreasonable assumption that the basic properties will be weakest for those esters which are derived from the strongest acids. In the case of the imidoesters such an assumption was unnecessary, as the affinity constants could be determined directly by means of the hydrolysis constants of the hydrochlorides as obtained from conductivity measurements. This similarity between imidoesters and the acid esters brings us to the last topic of our report.

X. *The Analogies between Imidoesters and Acid Esters.*

Our investigations have brought to light the following parallelism between imidoesters and acid esters:

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[1] See a later paper in This Journal, by Wm. McCracken.

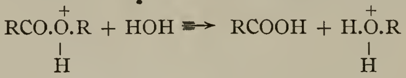
[2] Z. physik. Chem., **36**, 419 (1901).

(1) The decomposition of imidoesters by water, like that of ordinary esters, is accelerated by the presence of acids, and for both cases the (catalytic) acceleration may be ascribed quantitatively to the same cause, salt, and consequent ion, formation. For both decompositions the same fundamental isothermal velocity equation holds:

$$\frac{dx}{dt} = k_v \times C_{pos.ions} \times C_H \times C_{OH} \qquad (26).$$

In the case of the imidoester, a derivative of the ammonium ion is decomposed; in the case of the acid ester, it is an oxonium ion.

(2) In both cases the decomposition results in the formation of an ion of a stronger base than the original substance was; for the imidoester (equation 20), ammonium ions are formed from imidoester ions and ammonium hydroxide is a stronger base than the imidoester. For the acid ester we have,



$$\underset{\displaystyle H}{\overset{+}{\text{RCO.O.R}}} + \text{HOH} \rightleftharpoons \text{RCOOH} + \underset{\displaystyle H}{\overset{+}{\text{H.O.R}}} \qquad (27),$$

$$\rightleftharpoons \text{RCOOH} + \text{HOR} + \overset{+}{\text{H}} \qquad (28),$$

the oxonium ion of alcohol resulting, and alcohols unquestionably must form stronger oxonium bases than acid esters do.

(3) In both cases [illegible] velocities of decomposition are the greatest, the weaker the original base; the weaker imidoesters are decomposed much faster than the stronger ones, and the same is true, according to Euler, for the weaker basic acid esters (see above).

(4) This decomposition of imidoester ions by water is accelerated by electrolytes (salt effect), just as is the decomposition of the acid esters. In both cases we probably have to do with an increase in the ionization of water.

(5) Imidoesters, like acid esters, are decomposed (catalytically) by alkalis, and for both reactions the same fundamental equation,

$$\frac{dx}{dt} = K_v \times C_{neg.ions} \text{[illegible]} {}'_v \times C_{ester} \times C_{OH} \qquad (29),$$

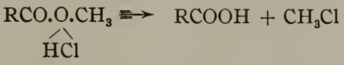
again holds, *i. e.*, the velocity of decomposition is proportionate to the concentrations of the ester and the hydroxyl ion. In both cases the velocity constants for decomposition in alkaline solution are greater than for acid solutions.

(6) Neighboring (ortho) alkyl groups interfere both with the esterification of the aromatic acids and with the saponification of their esters. Pinner found, likewise, that neighboring alkyl groups interfere with the formation of imidoesters from nitriles, and we have confirmed his results for *o*-tolunitrile and for *β*-naphtonitrile,[1] and have found, besides, that the decomposition by water of such an imidoester, once prepared from the silver salt of an acid amide, is also very perceptibly retarded by the neighboring group. For ethyl imido-*o*-toluylate the velocity constant is 0.00128, as compared with 0.00175 for the *p*-toluylate, whereas the *o*-toluylate, as the weaker base (the constants are 2×10^{-9} for the ortho and 2×10^{-8} for the para ester) ought to decompose the faster.

(7) Dry imidoester hydrochlorides are decomposed at ordinary temperature or by moderate heat, say at 120°–130°, into alkyl chlorides and acid amides, according to

$$\mathrm{RC(:NH_2Cl)O\overset{C}{H}_3 \rightarrow RCONH_2 + CH_3Cl} \qquad (30).$$

Dry acid esters, treated with hydrogen chloride, also give alkyl chlorides, according to



$$\mathrm{RCO.\underset{HCl}{O}.CH_3 \rightarrow RCOOH + CH_3Cl} \qquad (31).$$

The chief point of difference between imidoesters and acid esters lies in the more pronounced basic properties of the former and the formation of salts which are comparatively little hydrolyzed—a difference which is invaluable for the experimental study of catalytic action, but still is only a difference of degree and not of nature.

A reply to Mr. Acree's remarkable article in the January number of THIS JOURNAL will appear in the March number.

CHICAGO, September, 1907.

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[1] McCracken: *Loc. cit.*

ON SOME CUPRAMMONIUM SALTS. V.[1]

BY DAVID WILBUR HORN.

The object of the experiments described in this paper was to obtain definite information concerning the influence of the acid residues upon the complexity and stability of cuprammonium salts. The result of most general interest is the arrangement af 9 well-known acids in the order in which they favor the formation of copper-ammonia complexes.

Cuprammonium salts of the same degree of complexity containing different acid residues are not equally stable. This fact was pointed out in the second paper of this series.[2] The difference was illustrated by these salts:

$$CuSO_4 + 4NH_3 + H_2O,$$
$$Cu(NO_3)_2 + 4NH_3.$$

Reychler's values[3] for the molecular lowering of the freezing point and for the equivalent conductivity of these two salts in aqueous solution are quite different. There is a marked difference also in Blanchard's values[4] for the viscosity of their aqueous solutions and for the effect of ammonia upon it.

The cause of the differences might lie in the acid residue or in the "water of crystallization." The importance of this last factor could not be estimated. Experiment has shown that the union with the water is a most intimate one. The sulphate has been kept unchanged over lime for one year[5] and even in a vacuum over phosphorus pentoxide for a week at a time.[6] If it is heated to drive off the water, two ammonia groups leave the molecule at the same time.[7] To eliminate this uncertain factor, "water of crystallization," in my experiments, water was excluded.

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[1] Read in abstract at the meeting of the American Chemical Society at Toronto, June 28, 1907.

[2] THIS JOURNAL, **35**, 272 (1906).

[3] Ber. d. chem. Ges., **28**, 555 (1895).

[4] J. Am. Chem. Soc., **26**, 1315 (1904).

[5] Horn and Taylor: THIS JOURNAL, **32**, 267 (1904).

[6] Horn: *Ibid.*, **38**, 477 (1907).

[7] Sabbatani: Jahres. d. Chem., **1**, 960 (1897). Horn and Taylor: *Loc. cit.*, p. 272.

The guide in this work has been the Phase Rule. Definite and comparable results may be obtained, as has been shown,[1] by selecting one temperature for all of the experiments and preparing the salts, to be studied later, in systems where copper salt, ammonia, and water are always present in the same molecular ratio.

Any molecular ratio of the 3 components,

$$x \text{ mol } Cu(Ac)_n : y \text{ mol } NH_3 : z \text{ mol } H_2O,$$

may be selected, just as any temperature will do, provided it be maintained invariable throughout. I adopted a ratio in which $z = 0$ for the reason already given, *i. e.*, to exclude possible effects due to "water of crystallization." Any such ratio has the further advantage of experimental simplicity, for at all temperatures above the boiling points of the saturated solutions of the several cuprammonium salts in liquid ammonia the systems will consist only of a solid phase and a gas phase. In the solids, the ratio of the components will adjust itself automatically in accordance with the Law of Definite Proportions; and when this has occurred y may be maintained at a constant value very simply by working at any constant pressure.

Such a system, in which $z = 0$, is one of the limiting cases of a system originally ternary and divariant, containing one solid, one liquid, and one vapor phase, like those in which cuprammonium salts are usually prepared from aqueous solutions, and like the one worked out experimentally in considerable detail and described in the third paper in this series.[2] Since it is very doubtful if the last traces of water are ever excluded by observing any of the usual precautions, z probably never equals zero in my experiments but only approaches to it in value. The equality sign has been used in this sense. Although virtually the systems are binary when z becomes vanishingly small, there is no real gain in simplicity in so regarding them; for as the liquid phase disappears when the component water vanishes, they remain divariant at all temperatures above the boiling points of the saturated solutions of the several cuprammonium salts in liquid ammonia. On the other hand, there is a real loss in considering such systems as binary, for the ultimate relation to the more usual ternary systems which have yielded most of the cuprammonium salts is in this way obscured.

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[1] Horn: THIS JOURNAL, **37**, 475ff. (1907).

[2] *Ibid.*, **37**, *loc. cit.*

From both points of view, the method of study is the same. One must obtain different solid cuprammonium salts that exist *in stable equilibrium* with gaseous ammonia at some one temperature and pressure and then compare them as to complexity and stability. Since the systems all contain the same metallic element, copper, and the same gaseous substance, ammonia, under the same conditions of temperature and pressure, they are identical except as to the nature of the acid residue. The difference in properties, therefore, that the systems may exhibit can only be referred to the difference in the acid residues. The most striking differences actually exhibited by the systems are in the complexity and stability of the cuprammonium salts that appear as the solid phases when equilibrium exists in each of the systems. Consequently the complexity and stability must be functions of the nature of the acid residue. The word function is used in the same sense as in the statement that "the properties of an element are functions of its atomic weight."

The salt which, in equilibrium at the given temperature and pressure, has the largest number of ammonia groups in it, certainly contains that acid residue which is most favorable to the formation of complexes, while the salt that, under the same conditions, has the smallest number of ammonia groups in it, contains an acid residue least favorable to the formation of complexes. Between these limits must be placed the acid residues occurring in salts that, under the same conditions, contain an intermediate number of ammonia groups. Of all the acid residues occurring in several salts that, under the same conditions, are found to contain the *same* number of ammonia groups, the one most favorable to the formation of complexes occurs in the salt that is most stable, and the one least favorable to the formation of complexes in the salt that is most unstable.

The relations between complexity and stability and the nature of the salt, and the dependence of the final results on the choice of temperature and pressure are brought out clearly by the aid of a graph. For the ammonia compounds of each copper salt, the solid-solid-vapor lines, *i. e.*, those of the space model representing the entire system as binary, when projected on the temperature-pressure plane, will give curves resembling those in the figure. The graph is a diagrammatic representation of the "vapor pressure curves" or "curves of dissociation tensions" of the compounds of three different salts, the sulphate, sulphocyanate, and chloride. The general form of the curves is represented as the same in all cases and is identical with that of the ordinary vapor pressure curves of pure liquids, like water. This is a direct inference from Isambert's measurements[1] of the dissociation tensions of the ammonia compounds of a number of salts.

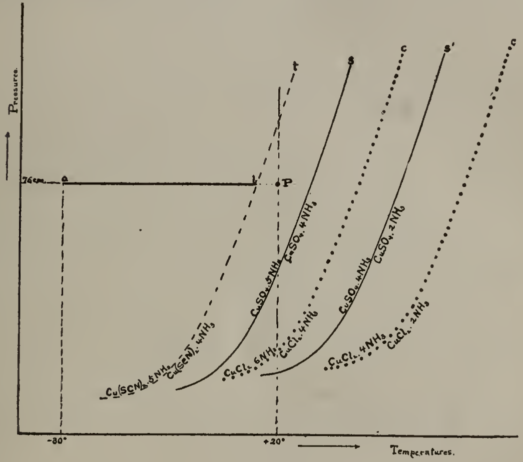

Fig. 1.

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[1] Compt. rend., **66**, 1259 (1868); **70**, 456 (1870). Ladenburg: Handwörterbuch d. Chem., **3**, 400.

Each curve in the diagram represents the pressures and temperatures of equilibrium between two solid cuprammonium salts and ammonia gas. The formulae of the two solids are written in each case along the curve. The areas between the curves represent the pressures and temperatures of equilibrium between one solid cuprammonium salt and ammonia gas. When the relative position of these curves with respect to each other and to the axes is known, all data concerning the preparation and relative stabilities of the anhydrous cuprammonium salts is at once available.

An area to the left of a curve represents the conditions for the stable existence of the more complex of the two salts written along the curve, and the area to the right of the same curve, the conditions of stability of the less complex one. To illustrate this, if anhydrous copper sulphate is placed in ammonia gas at a temperature and pressure represented by any point within the area to the left of the curve S, and to the right of the vertical axis erected at the boiling temperature of liquid ammonia, the pentammine sulphate must be formed. If the pentammine sulphate, still in contact with ammonia gas, is brought to a temperature and pressure represented by any point to the right of S or to the left of S′, it will decompose into the tetrammine sulphate.[1] If the pressure and temperature are maintained at values represented at the right of S′, the diammine sulphate[2] will be formed. When the curves are given, to know what will be the complexity of the ammonia compound that will be formed by a copper salt when placed in ammonia gas at some one temperature and pressure, it is only necessary to locate the point in the diagram that corresponds to the selected temperature and pressure and then to see within what area it lies. For example, when the temperature and pressure are such as to be correctly represented by a point located at P, it is evident at a glance that, under these conditions, a hexammine chloride, a pentammine sulphate, and a tetrammine thiocyanate would be formed, and that compounds of other than these degrees of complexity could have no stable existence until the conditions were changed from those represented by P to those represented by some other point in the diagram.

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[1] Bouzat: Ann. Chim. Phys. [7], 29, 330 (1903).

[2] *Ibid.*

The point P clearly represents an *arbitrary* selection of conditions, but if it is placed, as it has been, at the average laboratory temperature, +20° C., and the average atmospheric pressure, 76 cm., the selection need not be considered arbitrary because the point P then represents the conditions under which the larger number of chemical facts have been established and studied.

It is evident from the diagram that, if too high a temperature is selected for the experiments, in some cases P might fall on, or to the right of, the curve of the most complex ammonia compounds of one or more copper salts. In such cases compounds capable of existence would never enter into consideration, for they would remain undiscovered. It is a familiar fact that the highest ammonia compound of silver chloride remained unknown until Isambert happened to treat silver chloride with ammonia at temperatures *below* +20° C.; in this case, P, when representing atmospheric pressure and the average laboratory temperature, falls almost exactly upon the curve for the compounds $AgCl.2NH_3$ and $2AgCl.3NH_3$.[1] The diagram shows that the pentammine sulphocyanate would never have been discovered in the course of my experiments if they had all been made at the temperature of the room. The same is true of other compounds mentioned later.

To avoid being misled in such cases, and to make the basis of the work less arbitrary, I selected for my experiments atmospheric pressure and temperatures above the boiling points of the saturated solutions of the copper salts in liquid ammonia, about −30° C., and below the transition point at 76 cm. of the most unstable salt that could be dealt with conveniently with the facilities in this laboratory. These conditions are represented in the diagram by the heavy line, *ab*.

To illustrate the reasoning followed in arranging the acids in the order in which they favor the formation of copper-ammonia complexes, the data in the diagram may be used as follows: Hydrochloric acid, which appears in a hexammine salt, must be placed first, because no dissociation curve corresponding to a hexammine sulphate or thiocyanate exists at temperatures above −30° C. and pressures below 76 cm. Sulphuric acid must be placed before sulphocyanic acid, although both appear in pentammine salts, because the curves show that at any temperature the pentammine sulphocyanate, when dissociating, has a higher tension of ammonia over it than the pentammine sulphate, or, conversely, that at any pressure the pentammine sulphocyanate dissociates at a lower temperature than the pentammine sulphate. This method of reasoning is followed later.

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[1] Isambert: *Loc. cit.* Cf. Horstmann: Ber. d. chem. Ges., **9**, 756 (1876), and Horn: This Journal, **37**, 626 (1907).

The experiments described in this paper are not the first in which the action of ammonia on copper compounds has been investigated. Several isolated experiments of this kind had been carried out by others. The compounds that had already been made by the action of ammonia gas on anhydrous copper salts have the formulae:

$CuCl_2.6NH_3$,[1] $CuSO_4.5NH_3$,[2]
$CuBr_2.6NH_3$.[3]

A short time ago I described several new cuprammonium oxalates, obtained from solution, and the one of these with the largest number of ammonia groups has the formula $Cu(OOC)_2.5NH_3$.[4] In considering this along with the three other formulae just given, it was noticed that there are but 5 ammonia groups per molecule where the acid residue is dibasic, and 6 where the acid residue is monobasic. A similar relation was noticed in a comparison of the compounds of the same 4 salts with the smallest possible number of ammonia groups. The formulae of these compounds are:

$CuCl_2.2NH_3$,[5] $CuSO_4.NH_3$,[6]
$CuBr_2.2NH_3$,[7] $Cu(OOC)_2.NH_3$.[8]

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[1] H. Rose: Pogg. Ann., **20**, 155 (1830).
[2] T. W. Richards: Ber. d. chem. Ges., **23**, 3790 (1890).
[3] H. Rose: *Loc. cit.*, p. 150.
[4] This Journal, **35**, 279 (1906).
[5] Bouzat: *Loc. cit.*, p. 332.
[6] T. W. Richards: *Loc. cit.*
[7] Bouzat: *Loc. cit.*, p. 331.
[8] Horn: *Loc. cit.*, p. 276.

A *monammine* chloride or bromide can not be made from the corresponding *diammine* salt, although the monammine sulphate is made in that way.[1] When the diammine salts of either of the monobasic acids is heated in an endeavor to dissociate it into a monammine salt, the whole molecule is destroyed.[2]

Another example of the different influence of monobasic and dibasic acid residues was found in the ammonia compounds of cobalt and chromium. A dibasic acid residue appears not only in tetrammine salts analogous to the tetrammine salts containing two monobasic acid residues per molecule, as might be expected according to the ideas of Werner, but it also appears in *pentammine* salts.[3] These pentammine salts are *not* analogous to the pentammine salts containing one monobasic acid residue, *i. e.*, the purpureo salts. Werner and Gosling's statement[4] that *a dibasic acid residue may occupy two or one coördination places* does not explain this unexpected fact. It is *apropos* to remark that cases in which two monobasic acid residues together occupy one coördination place are not met with in the 110 groups of hexammine, pentammine, and tetrammine cobalt and chromium compounds that are now known.

It seemed most important, then, at the outset, to determine experimentally whether or not the largest number of ammonia groups that can combine with copper salts is a function of the *basicity* of the acid residue. The data for each copper salt are taken up under a separate heading. As my work has been interrupted for a time, many new facts besides those germane to the principal result of the investigation have been included under some of the headings.

I. Copper Sulphate.

Perhaps the most curious among the accumulated facts regarding cuprammonium salts is that copper sulphate has never been known to combine with more than *five* ammonia groups. The ideas of Werner cannot account for this fact[1] which is irreconcilable with all views based upon analogy. The pentahydrate Werner represented as $[Cu(H_2O)_4]SO_4.H_2O$, ascribing the presence of the fifth molecule to the affinity of sulphuric acid for water.[2] It is difficult to conceive of the existence of the anion which we must assume if the pentammine salt is represented by an analogous formula and is ionized:

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[1] Bouzat: *Loc. cit.*

[2] Bouzat: *Loc. cit.*, p. 332. T. W. Richards: *Loc. cit.*, p. 3790.

[3] $[Co(NH_3)_5.SO_4]X$. Jörgensen: J. prakt. Chem. [2], **34**, 262 (1885).
$[Co(NH_3)_5C_2O_4]X$. Jörgensen: Z. anorg. Chem., **11**, 418 (1896).
$[Co(NH_3)_5.SO_3]X$. Werner and Grüger: Z. anorg. Chem., **16**, 403 (1898).
$[Co(NH_3)_5.CO_3]X$. Werner and Goslings: Ber. d. chem. Ges., **36**, 2378 (1903).

[4] Werner and Goslings: *Loc. cit.*

$$[Cu(NH_3)_4]\ SO_4.NH_3 \rightleftarrows \overset{+\ +}{Cu(NH_3)_4} + \overset{=}{SO_4.NH_3}.$$

Mendelejeff evidently doubted the inability of copper sulphate to combine with more than 5 ammonia groups, for he states he convinced himself that no more than 5 groups can be added.[3] Bouzat found that the pentammine salt remained after anhydrous copper sulphate had been treated with an excess of liquid ammonia and the liquid allowed to boil off at atmospheric pressure.[4] But Mendelejeff does not state throughout what range of conditions he made the test, and the data for his experiments are not available. Bouzat's experiments do not prove that at temperatures *below* that of his laboratory more than 5 groups may not have been combined with the copper sulphate. Although the only other substance described, up to the time this work was begun, as a *pentammine* cuprammonium salt, *i. e.*, $CuBr_2.5NH_3$,[5] had been shown by T. W. Richards[6] to be a hexammine salt, yet a sulphate analogous to the hypothetical hexa-ammonia sulphate, namely, $CuSO_4.3[C_2H_4(NH_2)_2]$,[7] had been described by Werner.

A final answer can be given in all such cases by means of the method for determining transition points recently described.[8] When a thermometer is immersed in the mixture obtained by drawing anhydrous liquid ammonia upon an

[1] Horn: This Journal, **35**, 280 (1906).

[2] Z. anorg. Chem., **3**, 309 (1893).

[3] "Principles of Chemistry," Trans. 6 Russ. Ed., II., 363, footnote 35.

[4] *Loc. cit.*

[5] Rammelsberg: Pogg. Ann., **55**, 246 (1842).

[6] Ber. d. chem. Ges., *loc. cit.*

[7] Z. anorg. Chem., **21**, 219 (1899).

[8] Horn: This Journal, **37**, 619 (1907).

anhydrous copper salt, the system being so arranged that it communicates with the air only through a delivery tube dipping just beneath the surface of mercury, *i. e.*, so that a constant pressure of about 1 atmosphere is maintained, it is possible, by observing the thermometer, to tell whether the same solid compound existing at the temperature at which the saturated solution boils persists until the whole system has acquired the temperature of the room, or whether it decomposes to form a simpler one at intermediate temperatures. With constant pressure, as long as liquid ammonia is present the reading of the thermometer is constant, for the system is monovariant.[1] The instant the liquid disappears the system becomes divariant and the temperature begins to rise and continues to do so until the system acquires the same temperature as its environment, or until the system again becomes monovariant by the formation of another phase, *i. e.*, a new solid compound formed by the decomposition of the first compound. It is impossible for a new compound to be formed in such a divariant system without changing it to a monovariant one, thus causing a halt in the rise of temperature. Conversely, each halt in the rise of temperature after the liquid ammonia is entirely gone indicates a decomposition of a more complex into a less complex compound, and the absence of any such halt is *prima facie* evidence that the same compound that is stable at the temperature of the room is stable at the boiling point of the saturated solution in liquid ammonia.

The method followed in getting the data and interpreting them is very simple and is the same in all cases. It has already been sufficiently discussed.[2] Since the form of the curves is identical in all cases it is unnecessary to give the graph for every one. It is sufficient to state whether or not each case has been tested by this method, and if so, whether or not the curve indicated the persistence of a divariant system throughout the whole range included between the average temperatures of −30° C. and +20° C.

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[1] Two components: copper salt and ammonia: three phases: *solid* cuprammonium salt, saturated solution of cuprammonium salt in *liquid* ammonia, ammonia *vapor*.

[2] Horn: *Loc. cit.*

When the method was applied to copper sulphate and ammonia, the form of the curve was found to be that of a divariant system throughout. Therefore, *at all pressures not greater than one atmosphere and all temperatures between approximately* $-30°$ *C. and* $+20°$ *C.* the hypothetical hexammine sulphate is incapable of existence, and *copper sulphate cannot combine with more than 5 ammonia groups.*

When anhydrous copper sulphate is placed in dry ammonia gas there is often considerable difficulty in obtaining complete addition. Bouzat found that after six hours only 4.8 mol. of ammonia had been taken up, and we have found cases of incomplete addition after 16 hours. Upon the basis of a wide experience, which cannot be described here in detail, I attribute this to some impurity in the copper sulphate. I have found repeatedly that unless extraordinary precautions are taken to reduce the amount of iron present in the pentahydrate to a minimum, the anhydrous salt prepared from it is mixed with basic salts or other products of hydrolysis. I have tried removing four-fifths of the water at the boiling point of water, and also at the boiling point of alcohol, both at atmospheric pressure and at full vacuum of a good filter pump—about 2 cm.—and raising the temperature very gradually in some cases and very quickly in others. With the same range of conditions, I have tried removing the last molecule of water in an atmosphere of air previously passed through fuming sulphuric acid. In some cases a brownish product was obtained even when the salt, after repeated recrystallizations, was dehydrated by heating in contact with sulphuric acid of sp. gr. 1.84. Fusing with ammonium sulphate and volatilizing the excess of it[1] yielded a brownish product also. On the other hand, a copper sulphate containing but a few thousandths of a per cent of iron, such as "Kahlbaum's C. P.," yields a white anhydrous product when heated at atmospheric pressure in a current of dry air. When this is placed in dry ammonia gas at one atmosphere, it adds 5

[1] Klobb: Cmpt. rend., **114**, 836 (1892).

molecules of ammonia in somewhat less than 5 hours. The following are the analyses made in such an experiment:

Table I.—Analysis of the Anhydrous Copper Sulphate.

Weight taken for analysis. Gram.	Weight of cuprous sulphide found. Gram.	Percentage of copper found.	Percentage calculated for $CuSO_4$.
0.7896	0.3928	39.73	39.82
0.4395	0.2187	39.73	....

Table II.—Analysis of the Addition Product.

Weight taken for analysis. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuSO_4.5NH_3$.
0.2992	28.65	34.84	34.81
0.3612	34.50	34.75	....
	Weight of cuprous sulphide found.	Percentage of copper found.	
0.3472	0.1127	25.94	25.96
0.2722	0.0884	25.93	....

Mendelejeff is reported[1] to have stated that the pentammine sulphate does not lose any ammonia when placed over concentrated sulphuric acid. This is an error. Under such conditions this sulphate loses weight continuously for at least 3 months. Specimen data showing this are given below, in this paper.[2]

II. Copper Oxalate.

The principal question to be answered here is whether or not copper oxalate can combine with more than 5 ammonia groups.

Anhydrous copper oxalate has not yet been described. Hydrated copper oxalate cannot be completely dehydrated without further decomposition.[3] The crystallized pentammine oxalate,[4] although anhydrous when prepared from aqueous solutions, is extremely unstable and it is difficult, by this method, to obtain it pure, dry, and in a finely divided condition. Accordingly the anhydrous monammine oxalate[5] was used in these experiments. The best conditions for its preparation will be given in the next paper in this series.[1]

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[1] Ber. d. chem. Ges., **3**, 422 (1870).

[2] Page 200.

[3] Seubert and Rauter: Ber. d. chem. Ges., **25**, 2825 (1892).

[4] Horn: *Loc. cit.*

[5] *Ibid.*

When the monammine salt, $Cu(OOC)_2.NH_3$, is placed in dry ammonia gas, the color at once begins to change and the weight increases somewhat over 39 per cent during the course of 24 hours or more, after which it remains practically constant. The formation of the pentammine salt requires a gain in weight of 40.46 per cent. While the monammine salt is green, the addition product is purple-blue. It was analyzed, with the following results:

Weight taken for analysis. Gram	Volume of acid neutralized cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2.5NH_3$.[2]
0.2986	28.72	35.88	36.01
0.2106	20.69	35.66	....

When the transition point method was applied to mixtures of the pentammine oxalate obtained in this way and liquid ammonia, or to mixtures made by drawing liquid ammonia upon the monammine oxalate, the form of the curves, from about −30° C. up, was found to be that of a divariant system throughout. Therefore, *at all pressures not greater than one atmosphere and all temperatures between approximately −30° C. and +20° C., no more than 5 ammonia groups can be added to each molecule of copper oxalate.*

The source of dry ammonia gas that we used in the work with the oxalate is so generally useful for experiments when liquid ammonia is not available that it seems desirable to describe it briefly. Ammonia gas, obtained by warming ammonia water in a flask with a return condenser, was passed over some two meters of freshly broken potassium hydroxide and then through solid dry ammonium nitrate in a Drechsel bottle. The bottle was immersed in a mixture of ice and salt and water, and the outlet tube protected from moisture by a tube of freshly broken potassium hydroxide. Under these conditions the ammonia is absorbed to a large extent and the ammonium nitrate fuses. The resulting *solution*[1] can be made of any desired concentration, within certain limits, and can be so prepared as to furnish dry ammonia at any desired temperature, at a pressure proportional to the concentration. This holds true so long as the concentration of ammonia is so high that the solution is not saturated with ammonium nitrate. If the concentration is such that solid ammonium nitrate separates, or does not completely dissolve, the system is then monovariant and at each temperature can furnish the gas at but one pressure. This liquid, first described by Divers,[2] is most useful in studies of the addition of ammonia to solid salts as well as in many other experiments involving the use of dry ammonia gas. A good many measurements of the concentrations, temperatures, and pressures of this system are already available in the literature.[3]

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[1] VI. On Isomeric Oxalates.

[2] I am indebted to Miss E. Helen Lundie for making these experiments and the analysis.

We preserved this liquid by sealing it up in test tubes, which could be readily broken in suitable apparatus when desired. With sufficient care and attention to thermal insulation, it is possible to seal up solutions containing from 45 to 75 grams of ammonia to each 100 grams of ammonium nitrate. Of course, it is more convenient, where possible, to prepare the solution by adding anhydrous liquid ammonia to dry ammonium nitrate in a freezing mixture.

The form of apparatus represented in Figure II. proved very convenient. The vacuum desiccator contains the copper compound that is to be studied, in a weighing tube having a base of large area. The lid of the desiccator is held in position by bolts passing through two pieces of wood, as shown. The tube A contains the solution of ammonium nitrate in ammonia, sealed up in a test tube. The outlet 3 is connected to a good filter pump through a Drechsel bottle containing enough mercury to prevent the backward diffusion of water vapor. The whole apparatus is evacuated to the limit attainable by the pump, about 2 cm.; cocks 3 and 2 are then closed, and the tube A suddenly brought into a vertical position. The test tube breaks when it strikes the lower end of A, and A immediately fills with dry ammonia. Cock 2 is now opened cautiously and the whole apparatus allowed to fill with ammonia. Cock 2 is again closed, and the apparatus once more evacuated; then 2 is opened and the apparatus again filled with ammonia. When the ammonium nitrate solution no longer supplies ammonia at a sufficient pressure, as indicated by the manometer, cock 2 is closed, another tube, A′, containing a fresh test tube of solution is substituted for A, the pump is connected at *b* until A′ is evacuated, the test tube is broken as before, and the pressure in the whole apparatus brought to the desired point by proper manipulation of the cock 2. Cock 4 is kept closed except when making measurements of the pressure.

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[1] Kuriloff: J. russ. chem phys. Ges. [1], **25**, 170 (1893). Z. physik. Chem., **25**, 107 (1898).

[2] Phil. Trans., **163**, 359 (1873). Cf. Raoult: Compt. rend., **76**, 1261 (1873).

[3] Divers: *Loc. cit.* and Z. physik. Chem., **26**, 430 (1898). Raoult: *Loc. cit.* and Compt. rend., **94**, 1117 (1882). Troost: Compt. rend., **94**, 789 (1882). Kuriloff: *Loc. cit.*

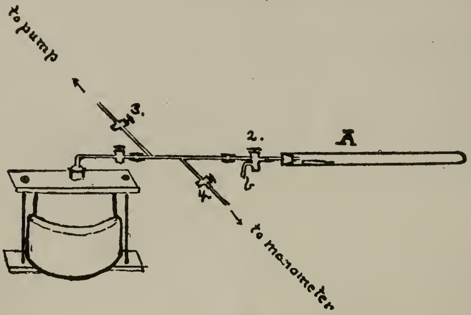

Fig. 2.

III. Copper Succinate.[1]

Anhydrous copper succinate was obtained by heating to constant weight at +150° C. the product obtained when hot dilute solutions of copper sulphate are added to hot dilute solutions of ammonium succinate. When placed in dry ammonia gas the color of the anhydrous salt at once begins to change and its weight increases somewhat over 46 per cent during the course of 18 hours or more, after which it remains practically constant. It is *essential* that the dehydration should be complete, and special attention must be given to this because it is difficult to dry the salt completely. Prolonged heating at +150° C. does not injure the succinate and does accomplish a complete dehydration. A specimen that had been exposed to the air several months increased only about 23 per cent in weight in dry ammonia gas, whereas 1.1763 grams of a dry specimen gained 0.5426 gram, or 46.13 per cent. The formation of the compound $Cu(OOC)_2C_2H_4.5NH_3$ from the anhydrous salt requires a gain of 46.46 per cent. The anhydrous salt is green; the addition product, purplish-blue.

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[1] I am indebted to Misses E. E. Van Wagner and E. H. Lundie for the experiments on the succinates.

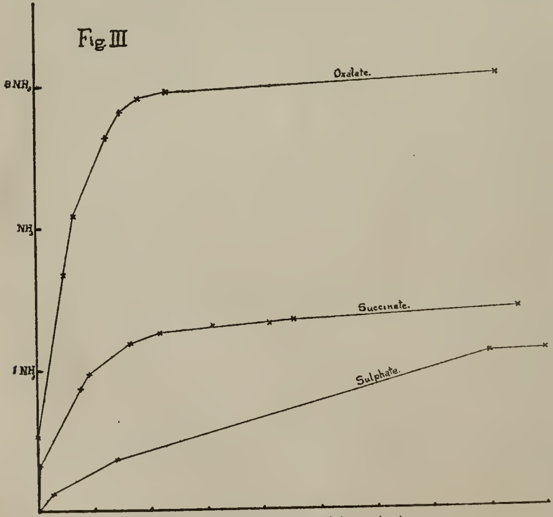
When the transition point method was applied to mixtures obtained by treating *this pentammine succinate* with liquid ammonia, this same salt *was found to be the only one that exists between approximately −30° C. and +20° C.*

The pentammine succinate, like the sulphate, loses ammonia in a desiccator over sulphuric acid, sp. gr. 1.84. The losses in weight exhibited by the pentammine sulphate, succinate, and oxalate after different lengths of time are given in the following table. The losses have been calculated in molecules of ammonia lost per molecule of salt. The specimens were in a finely divided state and were stirred at intervals with glass rods that were not removed from the weighing tubes throughout the whole time. The tubes were closed with ground glass stoppers during weighings. The original weight of sulphate was 1.207 grams; of succinate, 1.255 grams. In the case of the oxalate, after 0.2863 gram monammine oxalate had been exposed to the action of dry ammonia gas 14 hours, it weighed 0.3876 gram. If the exposure had been continued to constant weight the weight would have been 0.0154 gram more. As the subsequent treatment was to remove ammonia, it was not considered necessary to complete the addition before beginning the decomposition. Consequently 0.0154 gram was added to each loss in weight before the final calculations.

Sulphate.		Succinate.		Oxalate.	
Time in hrs.	Mols. lost.	Time in hrs.	Mols. lost.	Time in hrs.	Mols. lost.
6.5	0.12	1.0	0.32	0.0	0.53
34.0	0.36	19.0	0.87	1.5	1.67
192.0	1.11	22.0	0.97	2.0	2.09
216.0	1.13	40.5	1.18	3.75	2.64
240.0	1.16	52.5	1.25	4.5	2.82
264.0	1.18	87.0	1.30	5.5	2.91
288.0	1.20	99.0	1.32	7.0	2.96
350.0	1.21	109.0	1.34	24.5	3.08
438.0	1.28	205.0	1.42	...	....
486.0	1.29	....	....	...	....
2064.0	1.42	....	....	...	....

These data are represented graphically in Figure III.

The advantages of this graph are that the relative stabilities of the pentammine salts are apparent at a glance and



For sulphate and succinate, 1 unit = 1 day; for oxalate, 1 unit = 3 hours.

Fig. III.

that the existence of a sulphate, $CuSO_4.4NH_3$, a succinate, $Cu(OOC)_2C_2H_4.4NH_3$, and an oxalate, $Cu(OOC)_2.2NH_3$, is also indicated. The tetrammine succinate and the diammine oxalate[1] are new compounds. The tetrammine sulphate has been described by Bouzat[2] since the above data were obtained. The tetrammine succinate is of a pure, deep-blue color, lacking the purple shades of the pentammine salt.

A diammine succinate, $Cu(OOC)_2C_2H_4.2NH_3$, is formed when the pentammine salt is heated to constant weight in a current of dry air at about +90° C. The following results were obtained when the residue that had reached constant weight at +90° C. was analyzed:

Weight taken for analysis. Gram.	Weight of acid neutralized by the ammonia. Gram.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2C_2H_4.2NH_3$.
0.2036	0.09331	15.90	15.97
0.2009	0.09197	15.93	.....

An anhydrous diammine succinate was described by Schiff[3] in 1862 as the substance obtained in pseudomorphic crystals when a "dark-violet" succinate, "$Cu(OOC)_2C_2H_4.4NH_3$," gotten from solution, is heated on a water bath. Schiff's data consist in one analysis of the dark-violet crystals for copper oxide and in the percentage loss in weight shown by these crystals when heated on the water bath. Schiff's statement is erroneous.

The dark-violet succinate referred to forms so readily when copper succinate is dissolved in ammonia water that it is difficult to prevent its formation. Its color is distinctive, resembling that of potassium permanganate or violet chrome-alum, and is entirely unlike that of any other cuprammonium salt I have seen. When analyzed for ammonia the following results were obtained:

Weight taken for analysis. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2C_2H_4.4NH_3$.
0.1862	6.79	13.23	27.32
0.1228	4.61	13.61	.....
0.2251	8.47	13.66	.....
0.2019	7.66	13.77	.....

[1] See next paper in this series: On Isomeric Oxalates.

[2] *Loc. cit.*

[3] Ann. Chem. (Liebig), **123**, 45 (1862).

The percentage of ammonia found was only half of that required by Schiff's formula. To make sure that *all* of the ammonia in the compound had been determined, the substance was digested with concentrated sulphuric acid, to which phosphoric anhydride had been added, until the carbon was completely oxidized, and the residue then distilled as usual in our ammonia analyses. No blank was made for the nitrogen in the reagents. The following were the results:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2C_2H_4.4NH_3$.
0.2210	8.43	13.85	27.32
0.2311	8.86	13.91	.....

The percentage of ammonia required by the formula $Cu(OOC)_2C_2H_4.2NH_3.2H_2O$ is 13.67 per cent, and the analyses leave no doubt that this is the correct formula for Schiff's dark-violet "*tetrammine*" salt. The percentages of copper oxide calculated from the two formulae are 31.87 per cent and 32.11 per cent, so that Schiff's analysis agrees with either formula.

This dark-violet succinate yields, according to Schiff, the anhydrous diammine salt at 100° C. In several experiments at +100° C. a loss of about 15.3 per cent in weight was observed, whereas the loss of the 2 water groups should amount to only 14.42 per cent, and that of 2 ammonia groups to 13.67 per cent. The residue was a blue substance in pseudomorphic crystals, as described by Schiff. Even at the temperature of boiling alcohol, the loss was about 15.3 per cent, as is shown by the first of the three following analyses. In the last two, the method[1] of determining ammonia and water previously described was used at 100° C.

Weight taken for analysis. Gram.	Loss in weight on heating. Gram.	Total percentage loss on heating.	Weight of water collected. Gram.	Weight of ammonia collected. Gram.	Percentage of water lost on heating.	Percentage calculated for $Cu(OOC)_2C_2H_4.2NH_3 2H_2O$.
0.1567	0.0240	15.30	......	......	.....	.....
0.9682	0.1482	15.31	0.1424	0.0070	14.70	14.42
1.0014	0.1529	15.27	0.1446	......	14.44	....

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[1] Horn and Taylor: This Journal, *Loc, cit.*

These experiments show that when the compound $Cu(OOC)_2C_2H_4.2NH_3.2H_2O$ is heated to dehydrate it, some of the ammonia is expelled along with the water, and that Schiff's diammine salt, like the sulphates described by Kane, is a mixture.[1]

The dark-violet succinate can be obtained readily either by the spontaneous evaporation of an ammoniacal solution of copper succinate, or by the gradual addition of alcohol to this solution.

When the concentration of ammonia in the ammoniacal solution is sufficiently great, another succinate separates. This is a very soluble and unstable substance and, up to the present, I have not analyzed it.

When it had been found that the sulphate, succinate, and oxalate, all of which are salts of dibasic acids, are incapable of combining with more than 5 ammonia groups, attention was directed to salts of monobasic acids.

IV. Copper Chloride.

The well known hexammine chloride[2] was prepared from anhydrous copper chloride and dry ammonia gas. The anhydrous copper chloride was made from the crystallized dihydrate by heating to constant weight at +100° C. The dehydration is very readily accomplished within a couple of hours, although it has been denied[3] that this can be done at 100° C.

0.42016 gram of dihydrate attained a constant weight, 0.33174 gram, in 1.5 hours, the loss being 21.05 per cent, while that calculated from the formula is 21.13 per cent.

Bouzat has shown that the hexammine salt does not dissociate at atmospheric pressure until a temperature near +90° C. is reached. The transition point method, applied to the hexammine salt and liquid ammonia, showed that *the hexammine chloride is the stable form at all temperatures between the boiling point of its saturated solution in liquid ammonia*

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[1] *Ibid.*

[2] Rose: *Loc. cit.*

[3] Graham: Ann. Chem. (Liebig), **39**, 21 (1841).

and +20° *C.* In the same way the hexammine chloride was found to dissociate under about 2 cm. pressure at +46°.7 C.[1]

V. Copper Bromide.

The hexammine bromide[2] was prepared from anhydrous copper bromide and ammonia gas. In order that the addition may be complete it is essential that the bromide should be strictly anhydrous. Before use in our experiments, the bromide was finely ground in an agate mortar and kept over phosphorus pentoxide until it no longer lost weight. The neglect of some such precaution is probably the explanation of Rammelsberg's view that only 5 ammonia groups can be added to copper bromide.

The hexammine bromide, treated with an excess of liquid ammonia, was examined by the transition point method and found to be *the stable salt from the boiling point of its saturated solution in liquid ammonia to* +20° *C. at atmospheric pressure.* Under 2 cm. pressure, the hexammine bromide dissociates at +54.9° C.[3]

VI. Copper Iodide.

For these experiments, the compound $(CuI_2)_3.10NH_3$, described by Kohlschütter,[4] served as the basis. The general description of its preparation given by him is less satisfactory than the following explicit directions: Dissolve 30 grams pentahydrated copper sulphate in 100 cc. water and add 40 cc. ammonia water (sp. gr. 0.9). Dissolve 43 grams potassium iodide in 40 cc. water and add this to the ammoniacal sulphate solution. Then pass ammonia gas into the mixed solution, cooling gradually, until the solution is saturated with the gas at 0° C. In this way, most of the copper separates as the compound $CuI_2.4NH_3.H_2O$.[5] Collect this compound on a perforated porcelain plate with the aid of a filter pump, pressing it with a pestle to free it rapidly from the mother liquor. Place in a desiccator over freshly broken potassium hydroxide until dry. Prepare a water solution of this compound approximately saturated at ordinary temperatures and rapidly add 50 cc. of it, with constant stirring, to 38 cc. of water containing 50 grams potassium iodide. Filter this solution after half an hour to remove any tetrammine salt that may have separated. After 24 hours collect the compound $(CuI_2)_3.10NH_3$ and dry between filter paper and over potassium hydroxide

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[1] The temperature of the bath was 56° C.

[2] Rose: *Loc. cit.*

[3] Temperature of bath, + 62° C.

[4] Ber. d. chem. Ges., **37**, 1157 (1904).

[5] Berthemot: Jour. d. Pharm., **15**, 445. Rammelsberg: Pogg. Ann., **48**, 162 (1839). Kohlschütter: *Loc. cit.*

It is not essential that the tetrammine salt should be dried, but if the saturated solution is prepared from the salt after taking it from the funnel there is enough ammonia present to delay the separation of the compound $(CuI_2)_3.10NH_3$ for 72 or more hours.

Prepared under these conditions, the compound can be identified by its appearance. It resembles copper bromide or iodide very closely in color and general aspect. Its streak is brown, like that of limonite.

When finely ground it is acted upon by ammonia gas immediately, the brown color changing rapidly to green and later to blue. It is freely soluble in liquid ammonia, the solution yielding beautiful deep-blue crystals upon evaporation. These crystals are very stable as long as moisture is excluded, but they decompose with great rapidity when brought into the air and leave a brown to black residue. The following results were obtained in its analysis:

Weight taken for analysis Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuI_2.6NH_3$.
0.4803	34.06	23.58	24.38
0.3699	26.18	23.54	.. ..
0.4833	35.09	24.15	.....

When treated with liquid ammonia and examined by the transition point method *this hexammine iodide proved to be the stable compound at all temperatures between the boiling point of its saturated solution in liquid ammonia and +20° C. at atmospheric pressure.* At 2 cm., this hexammine salt dissociates at +67°.4 C.[1]

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[1] Temperature of bath, +76° C.

Although the chloride, bromide, and iodide combine with 6 ammonia groups, two other salts of monobasic acids that had received considerable attention, namely, the acetate and sulphocyanate, required further study before a generalization could be thought of. The diammine acetate and the tetrammine sulphocyanate were the most complex salts known in these cases.

VII. Copper Acetate.

The diammine acetate has been described by Foerster[1] and later by T. W. Richards and Oenslager.[2] The following method of preparation requires much less manipulation and gives a considerably better yield than any that had been given: Saturate 150 cc. 95 per cent alcohol with dry ammonia, cooling to keep it approximately at the temperature of the room. Add 20 grams finely powdered green monohydrated copper acetate, and pass ammonia gas into the solution for about ten minutes longer, allowing the solution to warm up in the meanwhile. Filter and set aside, exposed to the air, for about 15 hours. This supersaturated solution deposits, in this time, only a few crystals about its upper surface. Filter rapidly and shake. The diammine acetate separates immediately. Dry the salt between filter paper in a press and preserve in a desiccator over potassium hydroxide. The product was identified by the following analyses:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia.	Percentage ammonia found.	Percentage calculated for $Cu(OOCCH_3)_2.2NH_3$.
0.3581	17.07	15.86	15.82
0.2236	10.63	15.82	.....

The diammine salt increases in weight in ammonia gas, as found by Foerster, but the increase is more than the 12.8 per cent stated by him. The gain in weight of 0.6274 gram of the diammine acetate when kept in dry ammonia gas at the temperature of the laboratory and one atmosphere pressure is given in the following table. Column III. is especially significant in connection with Foerster's statement.

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[1] Ber. d. Chem. Ges., **25**, 3416 (1892).

[2] THIS JOURNAL, **17**, 305 (1895).

Time of exposure. Hours.	Total gain in weight. Gram.	Gain per hour. Gram.	Percentage gain in weight.	Percentage calculated for formation of $Cu(OOCCH_3)_2.4NH_3$.
24	0.0575	0.0024	9.17	15.82
45	0.0793	0.0010	12.65	.....
75	0.0874	0.0003	13.93	.....
144	0.0895	0.0003	14.26	.....

When liquid ammonia is drawn upon it the diammine acetate changes in color at once. If the ammonia is allowed to evaporate at atmospheric pressure while the substance warms up to the temperature of the laboratory, the addition product is the same tetrammine salt that is chiefly formed in the above experiment in ammonia gas. In the following analyses, 0.8607 gram of the addition product was weighed after it had been dropped into an excess of dilute sulphuric acid to prevent loss of ammonia, and the acid was then diluted to the mark on the neck of the 200 cc. measuring flask in which the substance had been weighed.

Volume solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOCCH_3)_2.4NH_3$.
48.14	16.99	27.27	27.31
48.10	17.03	27.36	.....
	Weight Cu_2S found. Gram.	Percentage of copper found.	
31.60	0.0434	25.50	25.45

These results furnish satisfactory proof of the existence of the tetrammine salt, $Cu(OOCCH_3)_2.4NH_3$, a conclusion which Foerster had drawn from his observation that the diammine salt increased 12.8 per cent by weight in ammonia gas. *The transition point method showed the existence of a yet higher acetate, i. e., one containing more than 4 ammonia groups per molecule, but it was not possible, with the facilities at hand, to establish its formula. It has a tension of 1 atmosphere when it dissociates at about —22° C.*

VIII. Copper Sulphocyanate.

The preparation of the diammine and tetrammine sulphocyanates has been discussed sufficiently in a previous paper.[1]

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[1] This series, III.

Either can be prepared pure without difficulty. The tetrammine salt used in these experiments was recrystallized twice from a very strong solution of ammonia in water by drawing a rapid stream of air through the solution. It deposited in the form of very small crystals. The diammine salt was obtained by exposing the mother liquors of the tetrammine salt to the air.

In the presence of water the direction of the reaction

$$Cu(SCN)_2.2NH_3 + 2NH_3 \rightleftarrows Cu(SCN)_2.4NH_3$$

depends upon the relative concentrations of copper sulphocyanate, ammonia, and water.[1] When there is no water present it depends upon the pressure of ammonia gas. At 1 atmosphere and ordinary temperatures, the tetrammine salt is formed. The diammine salt, under these conditions, attained a practically constant weight in about 18 hours.

Weight diammine salt taken. Gram.	Gain in weight. Gram.	Percentage gain in weight.	Percentage calculated for formation of $Cu(OOCCH_3)_2.4NH_3$.
0.2891	0.0452	15.62	15.95
0.5520	0.0863	15.63	.....

The transition point method showed the existence of a higher sulphocyanate dissociating at atmospheric pressure at about +10° C. It was impossible to weigh it for analysis by any of the ordinary methods. Accordingly, small pieces of apparatus, resembling distilling flasks in general form, were made from soft glass tubing. The side tubes were bent down at right angles and both the neck and side tube were constricted so that they could be sealed off quickly before the blast lamp. The experiments consisted in determining the increase in weight of the whole apparatus when liquid ammonia had been drawn upon a known weight of pure tetrammine salt contained in the bulb and the excess allowed to boil off. The whole apparatus, with the exception of the side tube, whose end dipped just beneath the surface of mercury, was kept surrounded with ice. The neck was sealed off immediately after the ammonia was introduced; and the side tube, when no more bubbles passed through the mercury.

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[1] Horn: *Loc. cit.*

The total weight of each piece of apparatus ranged from 11 to 14 grams. The results follow:

Weight tetrammine salt taken. Gram.	Gain in weight. Gram.	Percentage gain in weight.	Percentage calculated for formation of $Cu(SCN)_2.5NH_3$.
0.4367	0.0274	6.27	6.88
0.3786	0.0248	6.54	....
0.4332	0.0298	6.88	....

Evidently the composition of this new salt is represented by the formula $Cu(SCN)_2.5NH_3$. Its color is bluer and less purple than that of the tetrammine salt. It crystallizes in scales from boiling liquid ammonia, in which it is freely soluble. It is of special interest as the only known anhydrous *pentammine* copper salt of a *monobasic* acid, whether the addendum be ammonia or any of the other bases thus far shown to combine with copper salts. Its existence proves clearly and for the first time that the pentammine type is not conditioned by the presence of a dibasic acid residue.

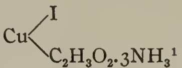
Diammine copper sulphocyanate dissolves freely in pyridine, as in liquid ammonia, and gives a dark olive-green solution from which emerald-green crystals gradually separate. They lose pyridine rapidly but can be quickly dried between filter paper and weighed for analysis without sensible decomposition. The following results were obtained in analyses for copper.

Weight taken for analysis. Gram.	Weight Cu_2S found.	Percentage copper found.	Percentage calculated for $Cu(SCN)_2.4C_5H_5N$.
0.2874	0.0456	12.66	12.82
0.2474	0.0392	12.65	.....

The composition of the salt can probably be represented by the formula $Cu(SCN)_2.4C_5H_5N$.

IX. Copper Acetoiodide and Acetobromide.

Some of the mixed cuprammonium compounds described by T. W. Richards and his students offered exceptional opportunities in efforts to determine the effect of the acid residue. Since copper acetate can take up but 4 ammonia groups at ordinary temperatures, and the iodide or bromide 6, it seemed especially interesting to determine whether or not the acetoiodide and acetobromide would combine with five, *i. e.*, the average of the four of the acetate and the six of the halide.

The compound  $Cu\begin{matrix}\diagup I\\ \diagdown C_2H_3O_2.3NH_3\end{matrix}$[1] was prepared as follows: 12 grams of the salt $Cu(C_2H_3O_2)_2.H_2O$ were dissolved in 50 cc. ammonia water (sp. gr. 0.9), the solution cooled, and then 30 cc. 57 per cent acetic acid, 6 grams ammonium iodide, and 50 cc. 95 per cent alcohol added separately in the order given. After being heated on the water bath the mixture gave a clear, deep-blue solution which was filtered and set aside exposed to the air. The crystals which separated were dried between filter paper and then over potassium hydroxide. They were analyzed for identification, with the following results:

Weight taken for analysis. Gram.	Volume acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuIC_2H_3O_2.3NH_3$.
0.2688	13.85	17.14	17.03
0.4257	21.52	16.81	.....

When the substance was treated with liquid ammonia an intensely colored solution and a deep-blue solid deposit were obtained. The solid was separated and the excess of liquid ammonia allowed to evaporate from it at atmospheric pressure while it warmed up to room temperature. The analysis was conducted as in the case of the acetate.

1.0970 grams were weighed in sulphuric acid and diluted to 100 cc. Portions of this solution were analyzed:

Volume solution taken for analysis. cc.	Volume acid neutralized by the ammonia.	Percentage of ammonia found.	Percentage calculated for $Cu(C_2H_3O_2)_2.4NH_3$.
24.03	21.64	27.30	27.31
23.13	20.83	27.30	.....
	Weight of Cu_2S found. Gram.	Percentage copper found.	
9.47	0.0333	25.57	25.45
8.65	0.0302	25.41	.....

Instead of being an addition product of the acetoiodide, this compound is evidently the tetrammine acetate previously described in this paper. The hexammine iodide is very soluble in liquid ammonia while the acetate is only slightly soluble, imparting but a faint color to the solvent. Apparently the liquid ammonia resolves the mixed molecule into its constituents as a result of this great difference in their solubility.

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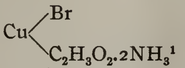
[1] Richards and Oenslager: This Journal, 17, 298 (1895).

The acetobromide,  $Cu\begin{cases}Br\\C_2H_3O_2.2NH_3\end{cases}$[1], was prepared as follows: Ammonia water (sp. gr. 0.9) was titrated against glacial acetic acid, and 10 cc. found to be equivalent to 7.41 cc. of the acid. Five grams anhydrous copper bromide (Kahlbaum) were treated with 10 cc. of the ammonia water, 7.3 cc. of the acetic acid, and 70 cc. 95 per cent alcohol in the order given. The resulting mixtures was heated on a water bath until the brown deposit that had formed was dissolved. The solution was then cooled under the tap to complete the separation of blue crystals that had begun before the heating. When analyzed for identification, the following results were obtained:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia.	Percentage of ammonia found.	Percentage calculated for $CuBrC_2H_3O_2.2NH_3$.
0.5048	21.85	14.40	14.42
0.4000	17.29	14.38	.....

When treated with liquid ammonia, a colored solution and a deep-blue solid were obtained. Two separate samples, A and B, of the solid were analyzed. 0.4438 gram A and 0.9295 gram B were weighed in sulphuric acid and the solutions diluted to 100 cc. The results follow:

	Volume of solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found.
A	23.86	9.08	28.53
	23.76	9.07	28.61
B	23.63	18.87	28.58
	17.58	14.01	28.52

		Weight Cu_2S found. Gram.	Percentage of copper found.
A	14.45	0.0189	23.56
	14.76	0.0189	23.03
B	8.63	0.0228	22.90
	8.79	0.0234	22.78

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[1] Richards and Shaw: This Journal, **15**, 644 (1893).

Hexammine copper bromide is much less soluble in liquid ammonia than the iodide, though considerably more soluble than the acetate. The composition of the solid indicates that it contained both salts. It is not possible, at present, to say finally whether in this solid I had a mixture or a compound. The ammonia determinations are to be given greater weight than those of copper in all cases where a halogen is present, and they indicate a solid of the same composition in the two cases. A mixture or compound of 1 mol. $CuBr_2.6NH_3$ and 3 mol. $Cu(C_2H_3O_2)_2.4NH_3$ requires 28.55 per cent ammonia and 23.65 per cent copper.

These experiments show that in all probability the mixed cuprammonium salts are quite different from the simple ones and are not to be regarded as substitution products derived from the latter. A study of the conditions under which these unique compounds exist in stable equilibrium in the presence of their components only is very desirable. They exist in hydrated as well as in anhydrous forms and, in three out of the nine known cases, exhibit the *triammine* type. The only other authentic case of this type among copper ammonia compounds is the cyanide, $Cu_3(CN)_4.3NH_3$,[1] in which, it will be noticed, the molecule is also a mixed one.

The study of salts of dibasic acids was next followed somewhat further, the dithionate, the orthophthalate, and the carbonate being used.

X. *Copper Dithionate.*

The anhydrous tetrammine dithionate described by Heeren[2] was prepared as follows: Pure manganese dioxide was obtained by heating the compound $Mn(NO_3)_2.6H_2O$ at +165° C. for 8 hours. After the dioxide had been washed, it was placed with water in a large Peligot tube and sulphur dioxide passed through the water until the manganese dioxide had dissolved. The manganese and sulphuric acid were then removed by using a very slight excess of barium hydroxide, and the solution of barium dithionate was added to a saturated solution of copper sulphate until barium sulphate was no longer precipitated. After filtering, the solution was evaporated to a small volume on a water bath and placed in a desiccator over sulphuric acid. The dithionate of copper gradually crystallized out. The crystals were dried between filter paper. Eight grams of the crystals were dissolved in 12 cc. water and treated gradually with 35 cc. ammonia water (sp. gr. 0.9). The cuprammonium dithionate is not very soluble under these conditions and separates in thin flat plates. It can be recrystallized from ammonia water and dried over potassium hydroxide. When analyzed for identification, the following results were obtained:

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[1] Schmidt: Jahres. d. Chem., **1898**, 1, 783. Malmberg: *Ibid.* Treadwell and Girsewald: Z. anorg. Chem., **39**, 84 (1904).

[2] Pogg. Ann., **7**, 189 (1826).

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found.	Percentage calculated for $CuS_2O_6.4NH_3$.
0.4859	33.90	23.21	23.38
0.3916	27.44	23.31	.....

The tetrammine dithionate is blue with a reddish cast. Its streak is lilac. When treated with liquid ammonia it acquires a blue color free from reddish shades and yields a product that gave the following results upon analysis. The first preparation was weighed as such while the second was dropped into sulphuric acid and weighed and the solution diluted to 100 cc.

I.	Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia. found.	Percentage calculated for $(CuS_2O_6)_2.9NH_3$.
	0.2530	19.13	25.15	25.55
		Weight Cu_2S found. Gram.	Percentage of copper found.	
	0.3318	0.0877	21.11	21.16
	0.3237	0.0860	21.21	.....

II.	Volume of solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated.
	23.79	15.17	25.14	25.55
	23.82	15.45	25.56	.....
		Weight Cu_2S found. Gram.	Percentage of copper found.	
	9.06	0.0205	21.37	21.16
	10.27	0.0232	21.37	.....

The formula $CuS_2O_6.4\frac{1}{2}NH_3$, or, more properly, $(CuS_2O_6)_2.9NH_3$, indicated by the analysis is not a simple one. It gives evidence of a condition within the molecule not unlike that which has been met with in the compounds $(CuBr_2)_3.10NH_3$ and $(CuI_2)_3.10NH_3$. This dithionate is very unstable at ordinary temperatures and dissociates with great rapidity in the air, yielding a lilac product that was shown, by the following analysis, to be the original tetrammine salt.

Weight taken for analysis. Gram.	Weight Cu_2S found. Gram.	Percentage copper found.	Percentage calculated for $CuS_2O_6.4NH_3$.
0.1452	0.0397	21.82	21.78
0.1731	0.0472	21.77	.....

The transition point method indicated that no higher compound than $(CuS_2O_6)_2.9NH_2$ *is formed at any temperature between that of the room and that of boiling liquid ammonia.* The dithionate is insoluble in liquid ammonia.

XI. Copper Orthophthalate.

Monohydrated copper orthophthalate was prepared as follows: 5 grams phthalic anhydride were dissolved in 1 liter of water and the solution boiled with 2.5 grams copper carbonate (Kahlbaum) approximating closely to the formula $Cu(OH)_2.CuCO_3$. The carbonate contained 56.2 per cent copper and 18.8 per cent carbon dioxide while the formula requires 57.5 per cent copper and 19.9 per cent carbon dioxide. The solution of copper orthophthalate, after boiling, was filtered and evaporated to 350 cc. on a water bath. After it had cooled, the copper salt, which separated, was collected and dried in the air. It was then dehydrated by heating to constant weight at +160° C. in an air bath, as directed by Hermann.[1] The blue salt changes to a deep olive-green in this process and loses about 7.2 per cent, the calculated amount of water being 7.3 per cent. Placed in ammonia gas it rapidly changes to a very dark blue, increasing about 33 per cent in weight. The formation of the compound $(Cu(OOC)_2CuH_4)_2.9NH_3$ requires 33.73 per cent gain.

When treated with liquid ammonia the same dark-blue color is developed and the product, when analyzed, gives results indicating this same formula.

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[1] Ann. Chem. (Liebig), **151**, 78 (1869).

0.7305 gram of the dark-blue product was weighed in sulphuric acid and the solution diluted to 100 cc. This solution was analyzed, with the following results:

Volume of solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $[Cu(OOC)_2C_6H_4]_2.9NH_3$.
23.09	12.67	24.99	25.22
24.33	13.38	25.04	.....
	Weight Cu_2S found. Gram.	Percentage copper found.	
9.30	0.0177	20.83	20.89
8.20	0.0157	20.87	.....

This orthophthalate, therefore, has a formula analogous to that of the highest dithionate, $[Cu(OOC)_2C_6H_4]_2.9NH_3$. *The transition point method, when applied to this substance, indicated the existence of a higher orthophthalate with a tension of 1 atmosphere when dissociating at about —8° C.*

XII. Copper Carbonate.

The diammine copper carbonate described by Favre[1] was prepared as follows: 50 cc. of a cold saturated solution of the solid "C. P. ammonium carbonate" of commerce was treated with 10 cc. ammonia water (sp. gr. 0.9) and then saturated with the same copper carbonate used in the preparation of the orthophthalate. About 6 grams copper carbonate were required. After the solution was filtered, 95 per cent alcohol was added slowly while the mixture was thoroughly shaken. The diammine salt separated in fine crystals that were pressed between filter papers and dried over potassium hydroxide. The following analysis served to identify it:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia.	Percentage ammonia found.	Percentage calculated for $CuCO_3.2NH_3$.
0.7812	49.94	21.26	21.64
0.7469	48.22	21.47	.....
	Weight Cu_2S found. Gram.	Percentage copper found.	
0.2917	0.1471	40.27	40.42
0.1793	0.0907	40.39	.....

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[1] Ann. Chim. Phys. [3], **10**, 116.

This diammine salt behaves as a *saturated* compound toward ammonia. Liquid ammonia may be boiled off from it for a period of at least one hour and the salt remains entirely unchanged. This case, with others, will be discussed in the next paper in this series.

Although other cuprammonium carbonates have been isolated in the course of this investigation, I have not yet succeeded in preparing any other anhydrous salt.

XIII. Copper Nitrate.

The tetrammine nitrate described by Kane[1] was prepared as follows: 10 grams crystallized hexahydrated copper nitrate were dissolved in 8 cc. water, and 25 cc. ammonia water (sp. gr. 0.9) then added. The mixture was heated until a clear solution was obtained and this was then shaken continuously and cooled in a stream of tap water. The crystals were dried over potassium hydroxide after they had been pressed between filter papers. When it was analyzed the following results were obtained:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc	Percentage ammonia found.	Percentage calculated for $Cu(NO_3)_2.4NH_3$.
0.5147	40.96	26.47	26.67
0.5425	41.60	26.43	.....
0.5522	42.27	26.39	.....
	Weight Cu_2S found. Gram.	Percentage copper found.	
0.3223	0.1002	24.83	24.85
0.3203	0.1002	24.98	.....

This nitrate is freely soluble in liquid ammonia and forms a more complex compound that has a pressure of 1 atmosphere when dissociating at about +15° C. This higher nitrate, like the pentammine sulphocyanate, cannot be analyzed by the ordinary methods. At first, bulbs were blown on test tubes and these were weighed empty and then with the tetrammine nitrate. Liquid ammonia was then drawn upon the salt, which dissolved completely. The test tubes were fitted with rubber stoppers carrying delivery tubes which were immersed in mercury to a depth of 20 cm. After all of the ammonia had boiled away, as indicated by the absence of bubbles rising through the mercury, the delivery tubes were raised almost to the surface of the mercury and the test tubes sealed off at constrictions made in them when the bulbs were blown. The bulbs and the parts of the test tubes removed in sealing were later weighed, with the following results:

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[1] Ann. Chim. Phys. [2], 72, 225, 337.

Weight tetrammine salt taken Gram.	Gain in weight found. Gram.	Percentage gain in weight.	Percentage calculated for formation of $[Cu(NO_3)_2]_4.23NH_3$.
0.4618	0.0514	11.14	11.67
0.3952	0.0445	11.25	.....

This highest nitrate, $Cu(NO_3)_2.5\frac{3}{4}NH_3$, or, more properly, $[Cu(NO_3)_2]_4.23NH_3$, has an almost sapphire-blue color whereas the tetrammine salt formed by its decomposition has a lilac color. In these bulbs there was a slight amount of lilac salt at places on the edges of the blue crystals. Accordingly apparatus of the kind used in determining the composition of the pentammine sulphocyanate was brought into use here. The excess of liquid ammonia was allowed to boil off at 1 atmosphere and 0° C. in these experiments, and the following results were obtained:

Weight tetrammine salt taken. Gram.	Gain in weight found. Gram.	Percentage gain in weight.	Percentage calculated for formation of $[Cu(NO_3)_2]_4.23NH_3$.
0.5238	0.0632	12.06	11.67
0.5131	0.0620	12.08	....
0.4706	0.0567	12.05	....

In these bulbs there was no other color to be seen but the sapphire-blue color. The results are slightly higher than required by the formula, but this may have been due to the retention of small amounts of mother liquor by the crystals. The total amount of ammonia in these specimens amounted to 34.56 per cent, 34.57 per cent, and 34.61 per cent, respectively, and the formula requires 34.33 per cent. The tetrammine nitrate is soluble in about its own weight of liquid ammonia and the sapphire-blue compound separates in thick plates. The apparatus was sealed when no more bubbles escaped through the mercury for five minutes, but further small amounts of occluded ammonia might have escaped had more time been allowed. All attempts to analyze the compound in the usual way yielded results that were not concordant, for the substance loses ammonia with extreme rapidity when exposed to the air.

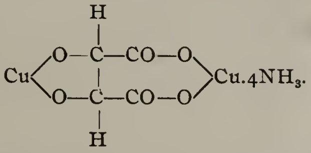
Examined by the transition point method, this system was found to be divariant from the time the liquid ammonia had boiled off until the lilac tetrammine salt appeared. It then became monovariant. It exhibited this same behavior from —41.°4 C. at 2.2 cm. pressure to +50.°3 C. at 234.7 cm. This is positive proof that the sapphire-blue substance is a definite compound. For if it were a mixture of two compounds, neither of which was the tetrammine salt, the system could never be divariant, but would be monovariant from the time the liquid ammonia had boiled off until the lilac salt appeared, and then it would become invariant. And if it were a mixture of two compounds, one of which was the tetrammine salt, the system would be monovariant throughout and the appearance of the lilac salt in visible quantity would in no way affect its degree of variability. The fact that the sapphire-blue substance crystallizes from complete solution in liquid ammonia makes the assumption that it is a product of incomplete addition very improbable. So far as the experiments go, they show that the sapphire-blue substance is a definite addition product of the tetrammine nitrate and that its composition is correctly represented by the formula, $Cu(NO_3)_2.5\frac{3}{4}NH_3$, or $[Cu(NO_3)_2]_4.23NH_3$.

Some progress had been made in similar studies of the chlorate, bromate, and perchlorate, but difficulties met with in the analysis of these compounds made it impossible to complete experiments before the work had to be given up.

A new tartrate that was prepared in the course of experiments directed toward obtaining an anhydrous diammine tartrate should perhaps be described in this place. It was formed when precipitated copper tartrate was treated with ammonia water (sp. gr. 0.9), and the mixture heated. The tartrate appeared to dissolve and crystallize out again in the form of the compound $Cu_2C_4H_2O_6.4NH_3.2H_2O$. The analysis resulted as follows:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found.	Percentage calculated for $Cu_2C_4H_2O_6.4NH_3.2H_2O$.
0.3661	18.28	18.12	18.08
0.3919	19.63	18.17	....
	Weight Cu_2S found. Gram.	Percentage copper found.	
0.4044	0.1713	33.82	33.67
0.3479	0.1470	33.75	....

This is evidently the hydrated form of the interesting tartrate described by Bullheimer and Seitz[1] and which is said to be formed in Fehling's solution, *i. e.*,



The hydroxyl hydrogen, as well as the carboxyl hydrogen, is replaced by copper or cuprammonium groups.

This tartrate resembles the crystallized anhydrous diammine oxalate very closely in color and in other respects.

XIV. Solubilities in Liquid Ammonia.

In the following list, the salts imparting no color to liquid ammonia are classed as insoluble, those imparting a faint color as slightly soluble, those an intense color as very soluble, and the rest as moderately soluble. The slightly soluble and moderately soluble salts are arranged from top to bottom in the order of increasing solubility.

Insoluble.

Sulphate
Oxalate
Succinate
Dithionate
Carbonate
Chloride

Slightly soluble.

Orthophthalate
Acetate

Very soluble.

Nitrate
Iodide
Sulphocyanate

Moderately soluble.

Acetobromide, with decomposition
Bromide
Acetoiodide, with decomposition

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[1] Ber. d. chem. Ges., **32**, 2347 (1899).

XV. Color.

In the course of the work upon which this series of papers has been based, I have prepared about 28 crystallized cuprammonium compounds and about half as many amorphous or pseudomorphic cuprammonium compounds of definite composition. Upon this basis it seems proper to make some statements as to the colors of these compounds. The general impression that all the salts containing 4 ammonia groups are of the same color is, in one sense, erroneous. The deep-blue color that has become familiar through the sulphate, $CuSO_4.4NH_3.H_2O$, is modified more or less by red or purple in every case. Each crystallized tetrammine salt can readily be distinguished by its color from any other one that is brought beside it, so far as I have been able to observe. Side by side comparison is not even required in some cases; for example, the tetrammine dithionate is so much redder than the tetrammine sulphate, and the tetrammine perchlorate[1] is so much less red than the sulphate that confusion would be impossible. The deep-blue colors of solutions of different tetrammine salts can likewise often be distinguished, in some cases without a side by side comparison.

If all of the red or purple modifications of the deep-blue color referred to are regarded as identical, this color is not characteristic of compounds containing 4 ammonia groups. The *pentammine* oxalate and the *diammine* acetate, for example, resemble the *tetrammine* sulphate more closely than does the *tetrammine* dithionate or perchlorate.

These statements concerning the solids refer to the reflected colors, but there are also differences in the body colors, or streaks.

Perhaps the greatest differences in color among salts of any one degree of complexity are found in the *diammine* salts. The dihydrated diammine succinate no more resembles in color the corresponding oxalate than potassium permanganate resembles crystallized copper nitrate. Among the anhydrous diammine salts, the oxalate is a brilliant sapphire, the carbonate a rich, deep, pure blue, the sulphocyanate a faded grayish-blue, and the acetate has a color resembling ordinary cuprammonium sulphate (tetrammine). The hydrated tartrate described above, in which the ratio $Cu:NH_3:H_2O$ is 1:2:1, resembles the anhydrous diammine oxalate so closely that a side by side comparison is necessary in order to distinguish them, while the ferrocyanide,[1] in which the same ratio, 1:2, occurs, is chocolate-brown. The anhydrous diammine acetate and the anhydrous diammine acetobromide differ almost as much in color as the familiar monohydrated tetrammine sulphate differs from ordinary pentahydrated copper sulphate.

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[1] Ann. Chem. (Liebig), **121**, 355 (1862).

It is a necessary conclusion, from the data at hand, that the color depends not only on the number of ammonia groups present but also on the acid residue. Because the color of all the hexammine, pentammine, and tetrammine salts that have been described is a more or less red modification of the same deep-blue color, one would infer that the effect of the ammonia upon the color overweighs that of the acid residue when the number of ammonia groups per copper atom is as great as 4. Because the diammine salts, on the contrary, exhibit a diversity of color, one would infer that when the number of ammonia groups per copper atom is not greater than 2, the effect of the ammonia is overweighed by that of the acid residue.

The effect of the acid residue upon the color, however, is not dependent upon the chemical nature alone of the acid, for one and the same acid may combine with the copper and ammonia in precisely the same ratio and yet yield products that are not identical in color. In the one case of this kind that I have met with, there is a difference in the molecular volumes of the two substances, which may mean a difference in the volume occupied by the acid residue, and this may be associated in some way with the difference in color.

It is scarcely conceivable that water molecules, when present, are without some effect upon the color, but I know of no cases where this is appreciable except in diammine salts of dibasic acids, and such cases cannot safely be used as data now because we do not know whether or not isomerization occurs when such molecules are hydrated or dehydrated.

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[1] **Messner: Z. anorg. Chem., 8, 368.**

XVI. The Acid Residues and the Formation of Complexes.

When the copper salts are arranged according to their valence, at atmospheric pressure and between −30° and +9°, toward ammonia, the following table is obtained:

	Valence toward ammonia.
CuI_2	6
$CuBr_2$	
$CuCl_2$	
$Cu(NO_3)_2$	5¾
$CuSO_4$	5
$Cu(OOC)_2C_2H_4$	
$Cu(OOC)_2$	
$Cu(SCN)_2$	
CuS_2O_6	4½
$Cu(OOCCH_3)_2$	4 (between −22° and +10°).

The hexammine salts dissociate at 2 cm. pressure at the following temperatures: Iodide, +67°.4; bromide, +54°.9; chloride, +46°.7. Therefore the iodide is the most stable, and the chloride the least stable.

The pentammine salts, when placed over sulphuric acid at the temperature of the laboratory, lose 1 molecule of ammonia in approximately the following lengths of time: Sulphate, 1 week; succinate, 1 day; oxalate, 1.5 hours. The pentammine sulphocyanate is less stable than these, for it dissociates at atmospheric pressure at about +10°, while they all dissociate at temperatures above +20°.

The copper salts that form hexammine and pentammine derivatives have been so arranged in the above table that the order indicates the relative stabilities of their ammonia compounds, as determined by the facts just mentioned.

This order into which the copper salts fall is unique among the experimental facts in the chemistry of metal-ammonia compounds. It is likely susceptible of more than one interpretation, and the following one is suggested merely because it seems as simple as possible. The equivocal meaning of the terms *affinity* and *valence* renders difficult any attempt at explaining this order and the situation does not seem to me to be relieved at all by adopting any of the modified terms derived from these two that have been proposed more or less recently.

Since the complexity and stability of the compounds have been determined under the same conditions of temperature and pressure in systems that differ from each other *only* in the chemical nature of the acid residue, it follows that the order of the salts of the acids given above must be the order of the acid residues themselves in their influence on complexity and stability.

If the idea of a force of attraction is adopted in dealing with these facts, although it may be questioned whether the existence of such a force acting through space from particle to particle has ever been demonstrated, the molecule of a copper salt exists as a result of the attractions between the copper atom and the acid residue. The attraction exhibited by the molecule of copper salt, when once formed, toward ammonia may be regarded as the resultant of the attractions between the copper atom and the acid residue. Whether the attraction exhibited by a copper atom toward an acid residue is assumed to be constant, or to depend upon the acid residue toward which it is exerted, the values of the resultants are proportional to the attractions of the acid residues. The acid residues, then, stand in the same order, with respect to their attractions toward copper, as do their salts in the table above. Whether such an attraction is *affinity* or not depends upon the definition of *affinity* adopted by the reader.

Whether or not it is assumed that this is *affinity*, it is interesting to compare the order with the results obtained by Ostwald in his studies on affinity. The acids are arranged in column I. of the following table according to the results with cuprammonium salts, in II. according to Ostwald's studies on the solution of calcium oxalate in mixed acids, in III. according to his work on the velocity of the hydrolysis of acetamide, in IV. according to the results obtained by him in the study on the saponification of methyl acetate, and in V. according to his investigation on the inversion of cane sugar.

I. −30° to +9°.	II.	III.	IV.
HI	HNO_3	HCl	HCl
HBr	HCl	HBr	HBr
HCl	HBr		HI
HNO_3		HNO_3	HNO_3
H_2SO_4		H_2SO_4	H_2SO_4
$C_4H_6O_4$	$C_4H_6O_4$	$C_2H_2O_4$	$C_2H_2O_4$
$C_2H_2O_4$		$C_4H_6O_4$	$C_4H_6O_4$
HSCN			
$H_2S_2O_6$			
	$C_2H_4O_2$	$C_2H_4O_2$	$C_2H_4O_2$

V.	VI. −22° to +9°.	VII. +11° to +14°.	VIII. +16° to +20°.
HBr	HI	HI	HI
$\left\{\begin{matrix}HCl\\HNO_3\end{matrix}\right\}$	HBr	HBr	HBr
	HCl	HCl	HCl
	HNO_3	HNO_3	H_2SO_4
H_2SO_4	H_2SO_4	H_2SO_4	$C_4H_6O_4$
$C_2H_2O_4$	$C_4H_6O_4$	$C_4H_6O_4$	$C_2H_2O_4$
$C_4H_6O_4$	$C_2H_2O_4$	$C_2H_2O_4$	$H_2S_2O_6$
	HSCN	$H_2S_2O_6$	HNO_3
	$H_2S_2O_6$	$HSCN_3$	HSCN
$C_2H_4O_2$	$C_2H_4O_2$	$C_2H_4O_2$	$C_2H_4O_2$

Apparently side reactions or other influences in Ostwald's experiments are sufficiently significant to make the order of the acids having nearly equal "affinities," HCl, HBr, HI and HNO_3, doubtful when determined by the methods he used. One difference, however, appears in the orders as determined by Ostwald's methods and by the cuprammonium salts; in the first, oxalic acid precedes succinic acid, whereas in the second the reverse is true.

But the order determined by the cuprammonium salts depends upon the temperature, as is readily seen in columns VI., VII., and VIII. If the changes in the attraction of a molecule of copper salt for ammonia with changes in external conditions is examined by the aid of Fig. I., it appears that at constant capacity, *i. e.*, valence, the intensity of the attraction of any one copper salt for ammonia, if measured by the value of the pressure of ammonia required to prevent dissociation, increases as the temperature falls. At constant intensity, the capacity or valence also increases as the temperature falls, but by steps or leaps. A curve of dissociation tensions represents the physical conditions under which the valence of a molecule of copper salt changes to another value, and the path of the curve represents the rate of change, with temperature, of the intensity of the salt's attraction for ammonia at the higher of the two valences represented along the curve.

If the order of the acid residues secured in the way that has been followed above is the same as the order of their "affinities," the work done so far seems to indicate the necessity for some new conception in the comparison of affinities, analogous in a sense to Van der Waals' "Coincident states" in gases. For it is clear that without some such conception the order of relative affinity will depend upon an arbitrary choice of temperature, and, therefore, that any such order must be regarded as an arbitrary rather than a natural order.

Another assumption that may be made in dealing with the facts given above is that the affinity of a molecule of a copper salt for ammonia is independent of external conditions. Raising the temperature increases the kinetic energy of the constituents and increases the distance between the centers of attraction, and thus reduces the intensity of the attractions that hold the compound together. This assumption brings into prominence the analogy between the change of dissociation tension with temperature in the case of a dissociating substance, and that of the vapor pressure with temperature in the case of a pure liquid. Such a method of consideration has this value, that it suggests the desirability of studying curves of dissociation tensions in order to see whether or not they end in "critical temperatures," beyond which the constituents could not be made to combine or to remain combined, no matter how great the pressure applied to them.

Whatever the value of these assumptions or any others that might be suggested, the experimental work will be pushed further. The corresponding order of the acid residues will be gotten by the study of other series of compounds, and similar studies will be made to determine the order in which the metallic atoms favor the formation of complexes. Curves of dissociation tensions will be studied from a more general point of view and through a much wider range of pressure.

ON THE VELOCITY CONSTANTS AND MECHANISM OF THE REACTIONS OF ALKYL HALIDES WITH URAZOLES AND URAZOLE SALTS.

[TWELFTH COMMUNICATION ON THE URAZOLES.[1]]

By S. F. Acree and G. H. Shadinger.

The following is a report of part of the work that is being carried on in this laboratory to learn the mechanism of the alkylation reactions involved when alkyl halides, sulphates, nitrates, potassium ethyl sulphate, and similar substances react with acids, bases, and salts, such as hydroxides, carbonates, nitrates, urazoles, and many others. We are studying the problem whether acids, bases, and salts enter into these reactions through their ions or molecules, or both. We are trying to learn how alkyl halides and other alkylating agents enter into these reactions.

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[1] This Journal, **27**, 118; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1, 258. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.

Do the alkyl halides dissociate, as Bruyn and Steger[1] assumed, into alkyl and halide ions which then react with other substances present?

$$KOH + C_2H_5I \rightleftarrows \overset{+}{K} + \overset{-}{OH} + \overset{+}{C_2H_5} + \overset{-}{I} \rightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

Do the alkyl halides unite with cations present, as Euler[2] assumed, and form complex cations which then react with other constituents of the solution?

$$KOH + C_2H_5I \rightleftarrows \overset{+}{K} + \overset{-}{OH} + C_2H_5I \rightleftarrows C_2H_5I.\overset{+}{K} + \overset{-}{OH} \rightarrow$$

$$\left\{\begin{array}{l} (1)\ \overset{+}{C_2H_5} + \overset{-}{OH} + \overset{+}{K} + \overset{-}{I} \\ \text{or} \\ (2)\ C_2H_5I.\overset{+}{K} + \overset{-}{OH} \end{array}\right. \begin{array}{c} \searrow \\ \\ \nearrow \end{array} C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

Do alkyl halides, nitrates, sulphates, hydroxides, cyanides, etc., dissociate, as Nef[3] assumed, into an unsaturated olefine or methylene derivative and the corresponding acid or water, which then react with other substances and yield the alkyl derivatives as end products?

$$C_2H_5I + KOH \rightleftarrows C_2H_4 + \overset{+}{H} + \overset{-}{I} + \overset{+}{K} + \overset{-}{OH} \rightarrow$$
$$C_2H_4 + \overset{+}{K} + \overset{-}{I} + HOH \rightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

Do the alkyl halides unite with the anions and form complex anions which decompose into the corresponding ester and halide ions?

$$KOH + C_2H_5I \rightleftarrows \overset{+}{K} + \overset{-}{OH} + C_2H_5I \rightarrow$$
$$\overset{+}{K} + C_2H_5I.\overset{-}{OH} \rightarrow \overset{+}{K} + \overset{-}{I} + C_2H_5OH.$$

In the present communication the problem is attacked by studying the action of alkyl halides on urazoles and salts of urazoles, hydroxides, thioacetates, etc. A series of alkyl iodides, bromides, and chlorides was used at different concentrations to learn the effect of change in concentration, and, at different temperatures to obtain the temperature coefficients. The thiourazoles and alkyl halides do not form appreciable amounts of 2-alkylurazoles, as do the corresponding oxyurazoles,[1] but yield apparently only the 3-thioesters:

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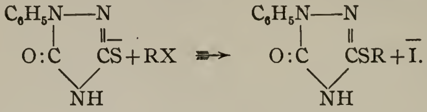
[1] Rec. Trav. Chim., **18**, 311.

[2] Ber. d. chem. Ges., **39**, 2726.

[3] Ann. Chem. (Liebig), **298**, 202; **309**, 126; **310**, 316; **318**, 1, 137; **335**, 191.



We investigated the question as to whether the anions of the urazoles, hydroxides, etc., or the undissociated substances, or both, react with the alkylating agents.

Various trials proved that the reaction goes to completion when the salt of the 1-phenyl-3-thiourazole and the alkyl halide (in slight excess) are allowed to react from two to four days. The reaction is then one of the second order, and if the anions react with the molecular alkyl halide the equation for the reaction velocity is

$$\frac{dx}{dt} = K_{trans} \times C_{anion} \times C_{alkyl\ halide} \qquad (1),$$

where K_{trans} is the reaction constant, C_{anion} is the concentration of the 1-phenyl-3-thiourazole anions, and $C_{alkyl\ halide}$ the concentration of the alkyl halide in gram molecules per liter. Under the conditions of the experiments the value of C_{anion} is always a definite fraction of the concentration of the urazole salt left in solution, and can be represented by $\alpha(A—x)$, in which α is the percentage of dissociation of the salt, A is the original concentration of the salt, and x the change in concentration of the salt. The differential equation then becomes

$$\frac{dx}{dt} = K_{trans}\,\alpha(A-x)(A-x) \text{ or } \frac{dx}{dt} = K(A-x)^2 \qquad (2)$$

when the alkyl halide and the urazole salt are originally present in the same concentration, A, and undergo the same change in concentration, x, in the time t. If the undissociated acid, base, or salt reacts with the molecular alkyl halide the equation for the reaction velocity is

$$\frac{dx}{dt} = K'_{trans} \times (I-\alpha)(A-x)(A-x) \text{ or } \frac{dx}{dt} = K'(A-x)^2 \quad (3).$$

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[1] Acree: This Journal, **37**, 71.

Since in these alkylation reactions the ionized and the undissociated portions of the urazole salt are always definite fractions of the concentration of the total urazole salt under given constant conditions, the concentration of the total salt can be substituted for the concentration of the ions or the undissociated salt in obtaining values for A, x, and $(A-x)$ in the equation $\frac{x}{t(A-x)} = AK$.

The equation therefore does not tell whether the total salt, the dissociated part, or the undissociated molecular part reacts. This question was settled by investigating the following problems:

1. The effect of adding a salt with a common ion and suppressing the ionization of the urazole salt.
2. The reaction velocity of different salts of phenylthiourazole. These different salts are dissociated to different extents and therefore have different reaction velocities.
3. The reaction velocity of the acid. This is less dissociated than the salt and so should have a smaller reaction velocity if it reacts through its ions.

The following problems also were studied:

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4. The effect of change of concentration.
5. The temperature coefficient.
6. Ionization of the salts in 50 per cent alcohol.
7. How do the alkyl halides react?
8. The effect on the velocity constant produced by the change of the halogen in the alkyl halides.
9. The effect on the velocity constant produced by the change of the alkyl group in the alkyl halides.
10. Similar results in analogous reactions which are ionic.

Let us first discuss the conditions attending the reaction between sodium 1-phenyl-3-thiourazole and an alkyl halide. If we start with a solution which is 0.2 normal with respect to the sodium salt and the alkyl halide and let the reaction proceed for some time, the concentrations of the sodium salt and of the alkyl halides are constantly becoming smaller. We might at first thought expect an increase in the percentage of dissociation of the urazole salt, corresponding to such dilution, and therefore expect an increase in the value of the velocity constant if the action is between the urazole ions and the alkyl halide, but a decrease in the value of the constant if the action is between the undissociated urazole salt and the alkyl halide. Such is not the case. Although the solution is 0.2 normal at the start, another salt, say sodium iodide, is formed, its concentration increasing as that of the sodium urazole salt decreases. The total number of gram molecules of the electrolyte present is a constant, 0.2, or the solution is always 0.2 normal with respect to the total amount of electrolyte. The work of Arrhenius,[1] Archibald,[2] and Jones[3] shows that the sodium urazole under these conditions can not change appreciably in percentage of dissociation. This follows from Arrhenius' theory that, since we have no accurate way of applying the mass law to such cases, the best way to approximate the ionization of two or more electrolytes in a solution is to assume that they share the solution between themselves in proportion to the concentration of each. For example, when half the sodium urazole is used up there is also an equal molecular amount of sodium halide formed. They then share the solvent equally and the amount of urazole left in half the solvent has the same concentration as before, 0.2 normal, and therefore is equally dissociated. This is true at any stage in the reaction, no matter what the concentration at the start.

1. As was said before, the value of the velocity constant obtained from any one set of experiments does not tell whether the action is molecular or ionic on the part of the urazole. After the addition of a certain number of molecules of sodium halide to the standard solution of sodium 1-phenyl-3-thiourazole, say 0.2 normal, the ionization of the urazole is no longer that of a 0.2 normal solution but corresponds to the new concentration which it must have in the presence of this added salt. For example, in 5 liters of solution contain 1 gram molecule of sodium 1-phenyl-3-thiourazole and 15 gram molecules of sodium iodide, the ionization of the

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[1] Z. physik. Chem., **2**, 288; **31**, 206.

[2] Trans. Nov. Sco. Inst. Sci., **9**, 101.

[3] THIS JOURNAL, **19**, 83; **22**, 5, 110; **25**, 349.

sodium urazole would be that of a 3.2 normal solution and not that of a 0.2 normal solution. The addition of the sodium iodide, then, causes a decrease in the ionization of the sodium urazole. If the reaction is between the urazole ions and the alkyl halide the reaction constant, expressed in the equation $\frac{dx}{dt} = K_{trans}\ \alpha(A-x)^2$, ought to decrease in direct proportion to the decrease in the percentage of dissociation of the sodium urazole. But if the action is between the undissociated molecules and the alkyl halide the reaction velocity, expressed in the equation $\frac{dx}{dt} = K'_{trans}(I-\alpha)(A-x)^2$, ought to increase with the increase in concentration of the undissociated molecular form. Of course these constants would be changed to some extent by the influence of the salts on the viscosity of the solution, by the hydration of the salts, both of which would have some effect on the velocity of the urazole ions, and *by any special catalytic action which the other salts might exert on the reaction.*

In all cases tried, a decrease in the value of the constant followed an addition of such an electrolyte to the urazole-alkyl halide solution. Apparently, then, the urazole ions react with the alkyl halide. When nonelectrolytes were added, however, there was no decrease but a slight increase, if anything, as is shown in Table II., experimental part. Electrolytes were added to solutions of sodium 1-phenyl-3-thiourazole and alkyl iodides, bromides, and chlorides, to barium 1-phenyl-3-thiourazole and ethyl iodide, to 1-phenyl-3-thiourazole and ethyl iodide, and to potassium hydroxide and ethyl iodide. *Since the constants decreased in all cases it seems that only the anions react with the alkyl halides.* See Tables II., VIII., X., XI., XII., XX., XXVII., XLI., and XLIII. in the experimental part.

Slator[1] got similar evidence that the action of sodium thiosulphate on the alkyl halides is ionic. He used ethyl bromacetate with that salt. The addition of a small quantity of silver nitrate decreased the activity of the thiosulphate because the silver nitrate rendered inactive that portion of the thiosulphate corresponding to the formation of $Na_3Ag(S_2O_3)_2$. The values of K so obtained approximated the value calculated for the sodium thiosulphate left unchanged. This result showed that the reactivity of trisodium silver thiosulphate is small compared with that of sodium thiosulphate and is negligible in the presence of a moderate excess of the latter salt.

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[1] J. Chem. Soc., **85**, 1286; **87**, 481. See also J. Chim. Phys., **4**, 565; **5**, 340.

When, however, an excess of silver nitrate was added the speed of reaction was only 0.05 of the original velocity. Slator thought that the complex salt dissociated thus:

$$Na_3Ag(S_2O_3)_2 \rightleftarrows 3\,\overset{+}{Na} + \overset{-\,-\,-}{Ag(S_2O_3)_2},$$

and

$$\overset{-\,-\,-}{Ag(S_2O_3)_2} \rightleftarrows \overset{-}{AgS_2O_3} + \overset{-\,-}{S_2O_3}.$$

The ions $\overset{-\,-\,-}{Ag(S_2O_3)_2}$ and $\overset{-}{AgS_2O_3}$ and the corresponding undissociated salts either do not react at all or at least very slowly. The uncombined thiosulphate is represented by $\overset{-\,-}{S_2O_3}$ ions, and probably the reaction depends upon their presence. Therefore, the slow activity following the addition of silver nitrate is strong evidence in support of the view that the reaction is primarily connected with the $\overset{-\,-}{S_2O_3}$ ion.

2. If the reaction of the 1-phenyl-3-thiourazole salts is ionic and independent of the nature of the cation, various metallic salts of the 1-phenyl-3-thiourazole should give reaction constants, the values of which are directly proportional to the percentage of dissociation of those salts at the same concentration. The value of K_1 for 0.2 normal sodium phenyl-3-thiourazole and 0.2 normal ethyl iodide is 0.36. The value of K_1 for the barium salt in the same concentration is 0.32. See Tables IV., VIII., and IX. in the experimental part.

In 0.05 normal solutions sodium chloride is dissociated 87 per cent, and barium chloride 75 per cent. The velocity constants for all reactions of the sodium and barium salts of the 1-phenyl-3-thiourazole agree very well with this amount of dissociation, but the constant for magnesium 1-phenyl-3-

Temp.	Urazole.	Alkyl halide.	K_1.	
25°	Sodium 1-phenyl-3-thiourazole	Ethyl iodide	0.35	(Table V.)
25°	1-Phenyl-3-thiourazole	" "	0.192	(" XXXV.)
50°	Sodium 1-phenyl-3-thiourazole	" "	3.28	(" VI.)
50°	1-Phenyl-3-thiourazole	" "	1.568	(" XXXIII.
25°	Sodium 1-phenyl-3-thiourazole	Methyl "	7.20	(" X.)
50°	1-Phenyl-3-thiourazole	" "	18.88	(" XXXIV.)

thiourazole is apparently high. Further work is needed with these salts. The evidence obtained, however, seems to show that the urazole anions react with the alkyl halides.

3. If the reaction is ionic, the free 1-phenyl-3-thiourazole acid, in reacting with an alkyl halide, should give a much lower velocity constant than its salt in the same concentration, since organic acids are, as a rule, much less dissociated than their sodium salts. The velocity constant should be proportional to the percentage of ionization of the salt or acid if the action is ionic, but proportional to the concentrations of the molecular form if the reactions are molecular and *if the substitution of sodium for hydrogen makes no difference in the reaction velocity.* The experimental data show that the velocity constant for the acid is much lower than that for the salt.

The velocity constants for the action of both ethyl and methyl iodides on the urazole acid decrease in value from the beginning. This is due to the formation of hydriodic acid, which suppresses the ionization of the urazole acid, and to the change of the 1-phenylthiourazole into the disulphide. The extent of the latter reaction and the value of the constant were studied in the usual manner. Since the reaction involves the ultimate union of two thiourazole anions, the formation of the disulphide must take place according to a reaction of the second order, whether the disulphide is formed directly from anions or from the undissociated thiourazole. Although a good constant was obtained for the reaction of the second order, there is no evidence on the question as to whether the anions or the undissociated thiourazole form the disulphide. This will be investigated. A 0.05 normal solution of 1-phenyl-3-thiourazole in 50 per cent alcohol gave a value of 0.0024 for K_1 (Table XXXVI.).

The evidence harmonizes completely with the assumption that the anions react with the alkyl halides.

4. The effect of change in the concentration of the reacting agents on the value of the velocity constant is now to be considered. The equation for a second order reaction shows that if the concentration becomes n times as great, the value

of the velocity constant is also n times as great. When equimolecular quantities of the two reacting materials are used the differential equation is $\frac{dx}{dt} = K(A-x)^2$. The integral of this equation is $\frac{x}{t(A-x)} = AK$, when the value of x is zero at the beginning of the reaction.

Now, if at the beginning of the reaction the concentration of the reacting substances were n times as great, the differential equation would become $\frac{dx}{dt} = K(nA-x)^2$. The integral of this equation is $\frac{x}{t(nA-x)} = nAK$ if the value of x is zero at the beginning of the reaction. The two integrals show that in the second case, in which the value of A is taken n times as great as it is in the first case, the value of the constant, nAK, is n times as large as the value of the constant AK in the first reaction. This statement does not bring into consideration the fact that a change in the percentage of dissociation accompanies a change in concentration. An increase in concentration causes a decrease in the percentage of dissociation. Therefore, when the concentration is doubled the value of the velocity constant becomes slightly less than twice the former value on account of this decrease in the dissociation. The following table gives some data bearing on this question, and the evidence is in harmony with all the other proof that the anions of the urazoles react with the alkyl halides.

Concentration of sodium 1-phenyl-3-thiourazole.	Concentration of C_2H_5I.	AK.
0.05 N	0.05 N	0.0099
0.10 N	0.10 N	0.0158
0.20 N	0.20 N	0.0361
0.40 N	0.40 N	0.0706

See Tables I., III., IV., and V. in the experimental part.

Burke and Donnan,[1] while studying the action of alkyl iodides on silver nitrate, likewise obtained changes in the value of the velocity constants with change of concentration, as is illustrated by the following table:

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[1] J. Chem. Soc., 85, 575, 578.

Initial concentration of both C_4H_9I and $AgNO_3$.	Mean velocity constant.
0.0500 N	0.00089
0.0250 N	0.00068
0.0200 N	0.00063
0.0125 N	0.00047

Initial concentration of both C_2H_5I and $AgNO_3$.	Mean velocity constant.
0.025 N	0.0022
0.0125 N	0.0015

5. A change in temperature has a great effect upon the velocity constant. Between 0° and 50° the mean temperature coefficient $(K_{t^\circ + 25^\circ}):K_{t^\circ}$ is 10.56. For sodium 1-phenyl-3-thiourazole and C_2H_5I the value of $K_{25^\circ}:K_{0^\circ}$ is 10.75 and of $K_{50^\circ}:K_{25^\circ}$ is 10.38. The average of these two is 10.56. Arrhenius' formula,[1] $\log K_T - \log K_0 = \alpha\left(\frac{1}{T_T} - \frac{1}{T_0}\right)$, gives a fair constant for α. Between 0° and 25° α is —3352. Between 0° and 50° α is —3615. Brigg's logarithms are used. For phenylthiourazole and C_2H_5I the value of $K_{50^\circ}:K_{25^\circ}$ is 8.17. See Tables I., VI., VII., XXXIII., and XXXV. in the experimental part.

It has been proven by Jones and West[2] and by A. A. Noyes[3] and Coolidge and coworkers that a change in temperature causes only a slight change in the percentage of dissociation. The increase in the reaction velocity, then, must be due to the increased velocity of the reacting particles in the solution, to the increased tendency of the particles to react when they come in contact with each other in the solution, and, without doubt, to other causes.

6. All results point to an ionic reaction on the part of the sodium 1-phenyl-3-thiourazole and the 1-phenyl-3-thiourazole, but the alkyl halides seem to react in molecular form.

Several theories have been advanced to explain the mechanism of the reactions of alkyl halides with other substances.

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[1] Z. physik. Chem., **4**, 226.

[2] THIS JOURNAL, **34**, 357.

[3] Z. physik. Chem., **46**, 323. J. Am. Chem. Soc., **26**, 134.

A. *The Theory of Lobry de Bruyn and Steger.*[1] These investigators supposed that in reactions between alkyl halides and other substances there is a very slight dissociation of the alkyl halide into alkyl and halide ions,

$$C_2H_5I \rightleftarrows \overset{+}{C_2H_5} + \overset{-}{I}$$

or

$$\frac{C_{ethyl\ ions} \times C_{iodide\ ions}}{C_{ethyl\ iodide}} = K_{ethyl\ iodide} \qquad (1),$$

and that the ions so formed then react with the ions of the other substance,

$$\overset{+}{K} + \overset{-}{OH} + \overset{+}{C_2H_5} + \overset{-}{I} \rightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I}. \qquad (1').$$

$C_{ethyl\ iodide}$ in equation (1) should be $(C_{ethyl\ iodide} - y)$, in which y is the concentration of the ethyl and iodide ions. y is so small that it can be neglected. Since the conductivity of alkyl halides in alcohol was found to be very small indeed, it was known by Bruyn and Steger that the percentage of dissociation of the alkyl halide can be only very small at most; they supposed, however, that a small amount of dissociation really exists and could account for all of the reactions. The small conductivity shown by alkyl halides in alcohol or water may be due to a slight decomposition into a halogen acid and an alkylene group, or to other reactions, as was shown by Lengfeld[2] and Hillyer,[3] working under Remsen.

It is quite true that if the reactions of the alkyl halides do depend on the primary and instantaneous ionization of the alkyl halide, only a small amount of this ionization might be necessary to give the reaction velocities actually found by experiment. We must recall that the percentage of dissociation of many of the double cyanides, potassium silver cyanide and potassium cadmium cyanide, for example, according to the expression

$$\overset{-}{Ag(CN)_2} \rightleftarrows \overset{+}{Ag} + 2\overset{-}{CN},$$

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[1] Rec. Trav. Chim., **18**, 325.

[2] THIS JOURNAL, **11**, 40.

[3] *Ibid.*, **8**, 251.

is less than 10^{-15}. Yet when a solution of one of these double cyanides is treated with hydrogen sulphide, the precipitation of silver sulphide or cadmium sulphide is complete almost instantaneously. This shows, then, that the mechanism of the reaction assumed by Bruyn and Steger is not without analogy. There is one fact, however, that the other workers in the field have apparently overlooked, and that is that the reactions of alkyl halides do not follow the requirement of the mass law as applied to the explanation given by Bruyn and Steger.

If the reaction between ethyl iodide and sodium 1-phenyl-3-thiourazole were really a reaction between ethyl ions and urazole ions, according to the expression

$$\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Ur}} + \overset{+}{\mathrm{C_2H_5}} + \overset{-}{\mathrm{I}} \rightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{I}} + \mathrm{UrC_2H_5} \qquad (2),$$

and if the ions are all formed practically instantaneously in comparison with the time required for the union of the ethyl and urazole ions, the velocity of the reaction would have to be expressed by the equation

$$\frac{dx}{dt} = K_{trans} \times C_{urion} \times C_{ethyl\ ion} \qquad (3).$$

In the equation (3) we can substitute $\alpha(A—x)$ for C_{urion} in which A is the original concentration of the urazole salt, x is the change in concentration of the salt in time t, and α is the constant percentage of dissociation of the salt. From equation (1) it is clear that we can substitute for $C_{ethyl\ ion}$ in equation (3) the value $K_{ethyl\ iodide} \times \frac{C_{ethyl\ iodide}—x}{C_{iodide\ ions}}$ or $K_{ethyl\ iodide} \times \frac{(A—x)}{\alpha_1 x}$, in which $K_{ethyl\ iodide}$ is the dissociation constant of the ethyl iodide, $C_{ethyl\ iodide}$ or A is the original concentration of the ethyl iodide, x is the change in the concentration of the ethyl iodide in the time t and hence is also the concentration of the sodium iodide at the time t, α is the percentage of dissociation of the sodium iodide, and $C_{iodide\ ions}$ or $\alpha_1 x$ is the concentration of the iodide ions, which come almost entirely from the sodium iodide. Equation (3) therefore becomes equation (4),

$$\frac{dx}{dt} = K_{trans} \times K_{ethyl\ iodide}\,\frac{\alpha(A-x)^2}{\alpha_1 x} = \frac{K(A-x)^2}{x}, \text{ or}$$

$$K = \frac{1}{t}\left(\operatorname{logn}\frac{A-x}{A} + \frac{x}{A-x}\right) \qquad (4),$$

if $x=0$ when $t=0$. But the application, in equation (4), of the data in Table I. in the experimental part leads to no constant value for K, and hence this interpretation of Bruyn and Steger's hypothesis is not in harmony with the experimental facts.

If we assume a very improbable case, namely, that the ethyl iodide dissociates very slowly in comparison with the union of the ethyl ions with the urazole anions, the velocity of the formation of the ethyl urazole would depend simply upon the rapidity of the ionization of the ethyl iodide. Since the velocity of the formation of the ionization products of the ethyl iodide would depend simply upon the concentration of the ethyl iodide, it follows that the velocity of formation of the ethyl urazole would be represented by the equation (5),

$$\frac{dx}{dt} = K(A-x) \text{ or } K = \frac{1}{t}\operatorname{logn}\frac{A}{A-x} \qquad (5),$$

in which A is the original concentration of the ethyl iodide and sodium urazole, and x is the change in concentration of the ethyl iodide or ethyl urazole in the time t. Equation (5), however, leads to no constants. It is just as improbable, further, that the entire reaction involves (1) a measurable rapidity of the ionization of the ethyl iodide, followed by (2) slow union of the ethyl and urazole anions. The equations corresponding to this case give no constants.

At the beginning of the reaction the concentration of the iodide ions is practically zero, because the ionization of the ethyl iodide can not be appreciable. But after the formation of even a small quantity of ethylurazole and sodium iodide the concentration of the iodide ions has become enormously large in comparison with the concentration of iodide ions furnished by the ethyl iodide alone. As a result of this the equilibrium of equation (1) would be disturbed, and since the C_{iodide} in equation (1) becomes very large the value of

$\frac{C_{ethyl\ ions}}{C_{ethyl\ iodide}}$ would become correspondingly smaller, and would constantly and greatly decrease during the reaction. Since the value of $\frac{C_{urion}}{C_{urazole\ salt}}$ does not change, it is evident that the value of K_{trans} in equation (3) would have to decrease enormously during the reaction. Such, however, is not the case. The value of K_{trans} has been found by many experiments to be practically a constant. It seems certain, then, that unless some further facts concerning the mechanism of the reaction are discovered in the future the hypothesis of Bruyn and Steger that alkyl halides react with other substances through primary dissociation into alkyl and halide ions, followed by the union of the alkyl ion and the anion, cannot be correct. The subject is under investigation.

B. *The bivalent-carbon hypothesis of Nef.*[1]—Nef, after exhaustive experimental work covering a period of years, came to the conclusion that alkyl halides, sulphates, nitrates, etc., alcohols, alcoholates, etc., all react with other substances only after they dissociate, to a very slight extent, into an unsaturated carbon complex and the other constituent composing the alkyl halide, sulphate, etc. There are two methods by which such a dissociation could take place; one would lead to the formation of a bivalent-carbon complex while the other would lead to the production of an olefine derivative:

$$CH_3CH_2I \rightleftarrows CH_3CH \rightleftarrows + HI,$$
$$CH_3CH_2I \rightleftarrows CH_2{=}CH_2 + HI.$$

Whether this equilibrium is between the molecular acid and the unsaturated carbon derivative as illustrated above, or between (amphoteric) ions, as illustrated in the following expressions, cannot be decided at present:

$$CH_3CH_2I \rightleftarrows \overset{+\,-}{C}H_3CH \rightleftarrows + \overset{+}{H} + \overset{-}{I},$$
$$CH_3CH_2I \rightleftarrows \underset{\downarrow}{\overset{+}{C}}H_2{-}\underset{\downarrow}{\overset{-}{C}}H_2 + \overset{+}{H} + \overset{-}{I}.$$

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[1] Ann. Chem. (Liebig) **298**, 202–374; **309**, 126; **310**, 316–335; **318**, 1–57, 137–230; **335**, 191–333.

Nef assumed that the ethylidine reacts with some other constituent, or rearranges into an olefine:

$$CH_3CH_2I + \overset{+}{K} + \overset{-}{O}C_2H_5 \rightleftharpoons CH_3CH \rightleftarrows + \overset{+}{H} + \overset{-}{I} + \overset{+}{K} + \overset{-}{O}C_2H_5 \longrightarrow CH_3CH \rightleftarrows + HOC_2H_5 + \overset{+}{K} + \overset{-}{I} \longrightarrow CH_3CH_2OC_2H_5 + \overset{+}{K} + \overset{-}{I}.$$

Although Nef had a large amount of experimental evidence in favor of this theory, he did not study the problem by the application of the mass law to the reactions. When this is done it is seen that there are some serious difficulties in making the facts harmonize with Nef's theory in its present form.

If Nef's latest interpretation[1] of the reactions between alkyl halides and phenylthiourazoles, for instance, were correct, and the only slow reaction were the union of the ethylidine and the urazole anion, we should have the following expressions:

$$UrH + C_2H_5I \rightleftharpoons \overset{-}{Ur} + \overset{+}{H} + CH_3CH \rightleftarrows + \overset{+}{H} + \overset{-}{I} \longrightarrow UrC_2H_5 + \overset{+}{H} + \overset{-}{I},$$

or

$$\frac{dx}{dt} = K_{trans} \times C_{urion} \times C_{ethylidine} \qquad (1).$$

Now, at the beginning of the reaction the amount of ethylidine and of hydrogen and iodide ions is very small, at most, and could be calculated from the equation (2),

$$\frac{C_{ethylidine} \times C_H \times C_I}{C_{ethyl\ iodide}} = K_{ethyl\ iodide} \qquad (2),$$

if the value of $K_{ethyl\ iodide}$ were known. But after the formation of even a small amount of the ethylurazole and hydriodic acid, the value of the concentration of the hydrogen and iodide ions, formed by dissociation of the hydriodic acid, becomes very large indeed in comparison with the value of the concentration of these ions furnished by the ethyl iodide alone. As a result, the value of the ratio $C_{ethylidine} : C_{ethyl\ iodide}$ must decrease correspondingly, and during the reaction become continuously smaller. Therefore, if Nef's theory were correct, the value of K_{trans} in equation (1) would decrease very greatly in value during the reaction. As a matter of fact it decreases only very slightly because of some secondary reactions, and, indeed, practically follows the equation

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[1] See Higley: Footnote, This Journal, 37, 296.

$$\frac{dx}{dt} = K_{trans} \times C_{urion} \times C_{ethyl\ iodide} \qquad (3).$$

Of course, the ratio $C_{urion} : C_{urazole}$ becomes smaller and smaller in equation (1) as the reaction proceeds, because of the suppression of the ionization of the urazole by the hydrogen ions from the hydroiodic acid formed in the reaction. Equation (3) takes this fact into consideration. The senior author of this communication is continuing the investigation of the mechanism of such alkylation reactions along physical chemical lines. It may be stated briefly here that we have not been able to harmonize Nef's theory with the experimental facts by assuming the following cases: (I.) A slow dissociation of the alkyl halide into an alkylidine and a halogen hydride, followed by a rapid or slow reversible or nonreversible union of the urazole ions or molecules with the alkylidine, or with the alkylidine and hydrogen ions, or with the alkylidine, hydrogen, and halide ions. (II.) An instantaneously reversible dissociation of the alkyl halide into an alkylidine and a halogen hydride followed by a fast or slow reversible or nonreversible union of the urazole ions or molecules with the alkylidine, alkylidine and hydrogen ions, or alkylidine, hydrogen, and halide ions. Our own work and that of Brusoff,[1] of Conrad, Hecht, and Brückner,[2] and of others, seems to show (1) that the olefine is formed by a direct loss of a halogen acid from the alkyl halide according to a monomolecular reaction, and (2) that the ester is formed from the urazole anion and the molecular alkyl halide according to a bimolecular reaction.

It seems that all the facts known at present warrant a serious doubt as to the validity of Nef's hypothesis as it is expressed at present. It may be shown later, however, by further study of the subject that certain factors not known at present must be considered, or that a modification of Nef's view may be in harmony with the truth. This subject will be discussed in great detail in a later article. Especially must it be borne in mind, however, that in such reactions as the above the *side products*, such as olefines, may be formed by independent side reactions, and not necessarily, as Nef assumes, by a change of a methylene residue into the olefine. The olefine is not necessarily an intermediate product in the alkylation reactions.

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[1] Z. physik. Chem., **34**, 129.

[2] *Ibid.*, **4**, 273, 631.

C. *The Complex-cation Hypothesis of Euler.*[1]—Euler, in a recent article, put forward the hypothesis that alkyl halides react with other substances, such as salts, because the alkyl halide first unites to a small extent with the cation and forms a complex cation, which then reacts with the anion:

$$C_2H_5I + \overset{+}{K} + \overset{-}{OH} \rightleftarrows C_2H_5I.\overset{+}{K} + \overset{-}{OH} \rightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I} \quad (1).$$

Euler did not subject the hypothesis to quantitative proof, and this has now been done by the writers. If equation (1) represented the true course of the reaction the following analysis would hold, whether the first or second, or both, steps in reaction (1) take place with measurable rapidity: the addition of 15 molecules of potassium iodide should cause only a slight lowering of the percentage of ionization of the potassium hydroxide present, but a very large increase in the amount of the complex cations, $C_2H_5I.\overset{+}{K}$, present at any moment, and hence should *increase* very largely the velocity constant of the reaction. Such, however, is not the case. The velocity constant of the reaction between the alkyl halide and potassium hydroxide is *lowered* by the addition of potassium iodide to just about the value calculated from the suppression of the ionization of the potassium hydroxide by the potassium iodide. The same holds true for a large number of other experiments along these lines. Furthermore, reference to Tables XLV. and XLVI. shows that the addition of ethyl iodide to an alcoholic solution of sodium phenylthiourazole hardly causes any change in the conductivity of the solution. If appreciable amounts of a complex cation or anion were formed the conductivity of the solution should be lowered considerably, since the ionic velocity of the complex cation or anion would be much less than that of the simple cation or anion. This quantitative evidence is not in harmony with Euler's hypothesis.

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[1] Ber. d. chem. Ges., 39, 2734.

D. *The Complex-anion Hypothesis.*[1]—As far as the evidence goes it seems that alkyl halide molecules react with the anions of the salts which are alkylated. It may be that the alkyl halide forms a very unstable complex anion, $C_2H_5I.\overline{X}$, which at once yields halide ions and C_2H_5X. Such an assumption must be tested further, however, by experiment.

That such a hypothesis is in harmony with the qualitative and quantitative facts can be shown very readily. Conductivity and other quantitative evidence shows that at most only a very small amount of the complex anion can be present at any instant. The question then arises whether the decomposition of this small amount of complex anion can account for the reaction. The treatment of the subject now depends upon whether the formation of the complex anion from the alkyl halide and urazole anion is a reversible reaction or not.

Taking the first of these two possibilities, let us see what are the quantitative relations if the formation of the complex anion from the alkyl halide and the urazole anion is a reversible reaction. The equilibrium would be represented by the following equation, in which $C_{alkyl\ halide}$ and C_X would represent the concentrations of the alkyl halide and the anions at any moment if no complex anion were formed from them, y or $C_{companion}$ the concentration of the complex anion, and K_{equil} the equilibrium constant:

$$C_2H_5I + \overline{X} \rightleftarrows C_2H_5I.\overline{X},$$

or

$$(C_{alkyl\ halide} - y)(C_X - y) = K_{equil}\, y = K_{equil}\, C_{companion} \qquad (1).$$

If y is very small, as it is in this case, no appreciable error is involved in writing equation (1) in the form

$$C_{alkyl\ halide} \times C_X = K_{equil} C_{companion} \qquad (2).$$

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[1] Acree and Johnson: This Journal, **38**, 262.

If, now, the complex anion yields the ester, the rate of formation of the ester must be directly proportional, at any moment, to the concentration of the complex anion, or

$$\frac{-d\,C_{companion}}{dt} = K_{trans}\,C_{companion} \qquad (3).$$

The small amount of complex anion, $-d\,C_{companion}$, changed in dt, is exactly equivalent to dx, the small amount of ester formed. If the complex anion decomposes very slowly in comparison with the rapidity of its formation, it is always practically in equilibrium with the alkyl halide and the urazole ions and we can substitute for $-d\,C_{companion}$ and $C_{companion}$ in (3) their equivalents dx and $C_{alkyl\ halide} \times C_X$. We then get

$$\frac{dx}{dt} = \underset{K_{equil}}{\underline{K_{trans}}} \times C_{alkyl\ halide} \times C_X \qquad (4).$$

see errata p. 823

If we started with the concentration $C'_{alkyl\ halide}$ of alkyl halide and C_{ursalt} of urazole salt at first, and x is the amount of ester which has been formed, and α is the percentage of dissociation of the urazole salt, then

$$C_{alkyl\ halide} = (C'_{alkyl\ halide} - x) \text{ and } C_X = \alpha(C_{ursalt} - x) \qquad (5).$$

We can therefore substitute for $C_{alkyl\ halide}$ and C_X in equation (4) their values in equation (5), and we then get equation (6),

$$\begin{aligned}\frac{dx}{dt} &= \underset{K_{equil}}{\underline{K_{trans}}}\,\alpha(C'_{alkyl\ halide} - x)(C_{ursalt} - x), \\ &= K(C'_{alkyl\ halide} - x)(C_{ursalt} - x) \qquad (6),\end{aligned}$$

see errata p. 823

which is exactly the relation found experimentally.

It is clear, then, that the alkyl derivative may come from a complex anion, which has been formed in small amounts from the alkyl halide and the anion in an instantaneously reversible reaction, provided that the complex anion decomposes very slowly in comparison with the rapidity of its formation from the alkyl halide and the anion. If the equilibrium in equation (1) is established only very slowly in comparison with the rapidity of the decomposition of the complex anion into the ester and halide ions, the equations representing such a course of reactions become practically identical with those in the next case to be considered.

Another set of conditions under which the esters could be formed from a complex anion in accordance with the established quantitative data is that in which the alkyl halide and anion unite slowly in an irreversible reaction and form a complex anion which decomposes very rapidly into the ester and the halide ions. The rate of formation of the complex anion is then

$$\frac{dx}{dt} = \frac{K_{trans}}{K_{equil}} \alpha(C_{alkyl\ halide} - x)(C_{ursalt} - x),$$
$$= K(C_{alkyl\ halide} - x)(C_{ursalt} - x) \qquad (7),$$

see errata p. 823.

in which x is the concentration of the complex anion formed in the time t, $C_{alkyl\ halide}$ and C_{ursalt} the original concentrations of the alkyl halide and urazole salt, respectively, and α the percentage of dissociation of the urazole salt. But if the complex anion decomposes very rapidly, the concentration of the ester formed, y, is practically the same as x, and no measurable error is involved in substitutimg y for x in equation (7). We therefore obtain (8) for the equation expressing the velocity of formation of the ester under the above conditions. *This equation is actually found to hold experimentally.*

$$\frac{dy}{dt} = K(C_{alkyl\ halide} - y)(C_{ursalt} - y) \qquad (8).$$

These consecutive reactions can not both take place with measurable slowness; the above equations would not express the progress of the reactions. We have discussed, therefore, three sets of conditions under which a complex anion, formed by the union of an alkyl halide and an anion, could yield the alkyl derivative and a halide ion.

If the dissociation of the alkyl halides were instantaneous, we could modify the hypotheses of Bruyn and Steger and of Nef so that they would hold experimentally. But such a modification would become identical with the complex-anion hypothesis discussed above.

If the urazole ions and *both* the alkyl and halide ions, or the urazole ions and the alkylidine, hydrogen, and halide ions, must first unite in an instantaneously reversible reaction and form a complex anion in small concentration, which then decomposes slowly according to the conditions discussed above, then the rate of formation of the ester must be expressed by the equation

$$\begin{aligned}\frac{dx}{dt} &= K_{trans} \times C_{companion}, \\ &= K_{trans} \times K \times C_{ethyl\ ion} \times C_{iodide\ ion} \times C_{urion} \text{ or} \\ K_{trans} &\times K \times C_{ethylidine} \times C_H \times C_I \times C_{urion}, \\ &= K_{trans} \times \underset{\text{omit.}}{\cancel{K}} \times C_{ethyl\ iodide} \times C_{urion}, \quad \text{see errata p. 823}\end{aligned}$$

which holds experimentally under all of the conditions known at present. But silver nitrate, potassium hydroxide, etc., do not react instantaneously with alkyl halides, and hence *the alkyl halides probably do not dissociate instantaneously, consequently even this modification of the hypotheses of Bruyn and Steger and of Nef does not seem to hold experimentally.*

That the alkyl halide molecules may react with the anions, however, is made probable from the fact, shown by Jones[1] and his coworkers, that neutral water forms hydrates with anions, and from the observations of Acree and Johnson[2] that acetone molecules react with hydroxylammonium ions, neutral water molecules with complex ester cations, neutral alcohol molecules with acetic acid cations, $CH_3COOH.\overset{+}{H}$, and water molecules with cane sugar cations, $(C_6H_{11}O_5)_2\overset{+}{O}H$. Acree and Nirdlinger[3] showed also that acetamide cations, $CH_3CO\overset{+}{N}H_3$, are hydrolyzed in water. All of these reactions are essentially alike.

If the alkyl halide forms an unstable compound with the anion it may be because of the unsaturated condition of the halogen of the alkyl halide or of the anion, or of both, and exactly the same reason may apply to the formation of the alkyl halide addition products of amines, dialkyl sulphides, R_2S, and other substances. That alkyl iodides react more readily than alkyl bromides, and these more readily than alkyl chlorides, may be due to the greater tendency of the iodine to react with or absorb the anions of other groups. The fact that primary, secondary, and tertiary alkyl halides decrease in activity in the order given may be connected with the so-called space interference, as well as with the reasons discussed above. The field is a ripe one for investigation and the work outlined above will be continued.

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[1] See H. C. Jones and coworkers "Hydrates in Aqueous Solution," Publication No. 60, Carnegie Institution of Washington.

[2] This Journal, **37**, 410; **38**, 308.

[3] *Ibid.*, **38**, 489.

7. Thus far all the arguments used to prove that the reaction between sodium 1-phenyl-3-thiourazole and alkyl halides is an ionic one on the part of the urazoles have been based on our knowledge of the behavior of an electrolyte in water solution. The reactions took place, however, in a 50 per cent ethyl alcohol solution, and the reaction constant is not the same as in pure water. That it is nearly the same, however, is proven by a study of the alkylation of sodium 1-phenyl-3-thiourazole by sodium chloracetate.

0.2 N sodium thiourazole + 0.2 N ClH_2COONa in water at 50°. $K_1 = 0.189$.

0.2 N sodium thiourazole + 0.2 N ClH_2COONa in 50 per cent alcohol at 50°. $K_1 = 0.15$.

See Tables XXXVII. and XXXVIII. in the experimental part.

Euler,[1] in his work on the action of chloracetic acid on silver nitrate, obtained results which were still closer.

Concentration in reaction mixture.		1000 K (80°).	
Chloracetic acid.	Silver nitrate.	Water.	45 per cent alcohol.
0.25	0.25	1.776	1.766
0.125	0.25	1.82	....
0.25	0.125	....	1.77
0.20	0.20	1.80	1.80

It is clear, then, that the fact that 50 per cent alcohol was the solvent used does not detract in the least from the validity of the evidence that the reaction is one between the urazole anions and the molecular alkyl halide.

8. When the alkyl group is the same, the velocity constant varies with the change of the halide in this order: for the

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[1] *Loc. cit.*

iodide it is greater than for the bromide, and greater for the bromide, in turn, than for the chloride. This agrees with the results of other investigators whose work will be given later. The following table is a summary of the velocity constants (at 25°) of the reactions described:

Alkyl (normal).	Halide.			Ratio.		
	Iodide.	Bromide.	Chloride.	Iodine.	Bromine.	Chlorine.
CH_3	7.20	.....	.....	...	....	.....
C_2H_5	0.316	0.117	.....	1	0.37	.....
C_3H_7	0.201	0.076	0.00130	1	0.38	0.093
C_4H_9	0.214	0.074	0.00364	1	0.35	0.017

Slator[1] got similar results in the reaction of sodium thiosulphate on the monohalide acetates.

Values of velocity constants at 25°.

	Ethyl iodoacetate.	Ethyl bromacetate.	Ethyl chloracetate.
	7.00	6.40	0.06
Ratio.	Iodine.	Bromine.	Chlorine.
	1.000	0.914	0.0086

Slator[2] obtained the following ratios from the action of alkyl halides on sodium thiosulphate:

Alkyl.	Iodine.	Bromine.	Chlorine.
CH_3	1	1	0.0025
C_2H_5	1	0.62	(very small)

Menschutkin[3] got the following ratio from the action of allyl halides on organic amines:

Iodine.	Bromine.	Chlorine.
1	0.166	0.00166

It is evident, then, that our results are in harmony with those of other investigators and show beyond question that the alkyl iodides have the highest reactivity. Closely following, however, in their reactivity, come the alkyl bromides, while the alkyl chlorides lag far behind.

9. The following table shows how the values of the velocity constants, in the reactions of alkyl halides with sodium thio-

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[1] J. Chem. Soc., **87**, 481.

[2] *Ibid.*, **85**, 1287.

[3] Z. physik. Chem., **56**, 52.

urazole at 25°, vary with the character of the alkyl group. Read down.

Table A.

	Halide.		
Alkyl.	Iodide.	Bromide.	Chloride.
Methyl	7.20	....	....
Ethyl	3.16	0.1170	....
n-Propyl	0.20	0.0764	0.00130
n-Butyl	0.214	0.0742	0.003640
n-Hexyl	0.0094	.....	....
n-Octyl	0.0159	.....	....
n-Cetyl	0.00132	.....	....
Isoamyl	0.0464	0.03560	0.001070
Isopropyl	0.0222	0.00626	0.000800
Isobutyl	0.0085	0.00640	0.000290
Tert. butyl	0.00088	0.00110	0.00055

The value of the constant varies greatly with the constitution in an isomeric series. In general, the secondary alkyl halide is less reactive than the primary, and the tertiary less reactive than the secondary. It will be noticed in Table B that the reactivity of the tertiary butyl iodide, bromide, and chloride does not decrease in the order given, as is generally found with the alkyl halides. In general, one must expect the relative reaction velocities of the different alkyl halides to vary with the nature of the substances with which the alkyl halides react.

Table B.

Alkyl.	Iodide.	Bromide.	Chloride.
n-Butyl	0.21400	0.07400	0.00364
Isobutyl	0.00850	0.00640	0.00029
Tert. butyl	0.00088	0.00110	0.00055

In the normal series the constant decreases with increase in the weight of the alkyl group, but the decrease is not nearly so large as that caused by the complexity of the group (side chains). Compare Tables A and B, above. It is evident that the so-called space interference may play the same rôle in these reactions that other investigators have noticed in entirely different reactions. In order to show the general relations, a resumé of some of the more important researches dealing with, or showing, the so-called space interference is made in this section.

Wislicenus[1] studied the action of alkyl iodides on ethyl sodium acetoacetate in ethyl alcoholic solution and obtained the following results:

Table C.

Iodide.	Relative velocity.
Methyl	196
Ethyl	21
n-Propyl	5
Isopropyl	1–9
Tert. butyl	(very small)
Allyl	784+

Menschutkin[2] obtained the following results with triethylamine in acetone solution at 100°:

Table D.

Iodide.	Relative velocity.	Iodide.	Relative velocity.
Methyl	1140.00	*n*-Butyl	1.38
Ethyl	10.10	*n*-Heptyl	1.08
n-Propyl	1.93	*n*-Octyl	1.00

Menschutkin also obtained the following results in his work on triethylamine and alkyl halides in acetone solutions:

Table E.

Alkyl.	Iodide.	Bromide.	Alkyl.	Iodide.
Ethyl	0.0608	0.00958	*n*-Butyl	0.00832
n-Propyl	0.0116	0.00165	Isobutyl	0.00191
n-Butyl	0.0083	0.00123	*n*-Propyl	0.0116
n-Heptyl	0.0065	0.00119	Isopropyl	0.00121
n-Octyl	0.0060	0.00110		

Hecht, Conrad, and Brückner[3] worked with alkyl iodides and sodium ethoxide in ethyl alcoholic solution at 30°, and obtained the following results:

Table F.

Iodide.	Relative velocity.	Iodide.	Relative velocity.
Methyl	61.72	Isopropyl	0.92
Ethyl	4.87	*n*-Heptyl	1.04
n-Propyl	1.71	*n*-Octyl	1.00

[1] Ann. Chem. (Liebig), **212**, 239.

[2] Z. physik. Chem., **5**, 589.

[3] *Ibid.*, **4**, 273, 631.

Burke and Donnan[1] worked with alkyl iodides and silver nitrate and found the relative reaction velocities to decrease in the following order: isopropyl, ethyl, *n*-propyl, methyl, *n*-butyl, isoamyl, isobutyl.

Slator[2] studided the action of sodium thiosulphate on the esters of monohalogen substitution products of acetic acid.

Table G.

Halide substitution product.	Relative velocity.
Ethyl iodoacetate	118.64
Ethyl bromacetate	108.47
Methyl bromacetate	99.15
Ethyl chloracetate	1.017
Methyl chloracetate	1.00

Menschutkin,[3] in his work on the influence of chemical constitution on the speed of esterification, has obtained results which, in general, are analogous:

Table H.

Primary alcohols.	Initial velocity.	Relative velocity.	Limit of esterification.
Methyl	55.60	.....	67.52
Ethyl	46.95	70.52	66.57
Propyl	46.92	70.18	66.85
Butyl	46.85	69.61	67.30
Octyl	46.59	64.40	72.34
Isobutyl	42.36	66.66	67.38

Acids with primary radicals.

Table I.

Acid.	Initial velocity.	Limit of esterification.
Formic	61.69	64.23 at 100°
Acetic	44.36	67.36 at 155°
Propionic	41.18	68.70 at 155°
n-Butyric	33.25	69.52 at 155°
n-Caproic	33.08	69.81 at 155°
n-Caprylic	30.86	70.87 at 155°

From the above work the following conclusions were drawn by Menschutkin:

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[1] J. Chem. Soc., **85**, 555.

[2] *Ibid.*, **87**, 481.

[3] Ann. Chem. (Liebig), **195**, 334; **197**, 193. Ann. Chim. Phys., [5], **23**, 14. Ber. d. chem. Ges., **10**, 1728; **11**, 679, 1507, 2117, 2148. Compt. rend., **105**, 1016.

(1) "The primary alcohols possess the highest limit of esterification and the greatest initial velocity. In the series given in Table H the velocity and limit vary regularly with the molecular weight."

(2) "The initial velocity and limit of the secondary alcohols are less than the primary alcohols; analogous differences in composition correspond with analogous differences of esterification."

(3) "The velocity and limit of the tertiary alcohols are very small, and they decompose during esterification."

(4) "The primary monobasic acids possess the smallest limit of esterification and the highest initial velocity. In the series given in Table I the limit and velocity vary regularly with the molecular weight of the acid."

(5) "The secondary acids show smaller initial velocities but higher limits of esterification than the primary acids; the effect of variation of composition is not marked."

(6) "The tertiary monobasic acids, whether of the fatty or aromatic series, are characterized by the smallest velocity, but by the highest limit of esterification."

Esterification of Aromatic Acids.

This work was done by Victor Meyer[1] with Fischer's method for esterification. The work, in general, gave valuable results as to the influence of chemical constitution on the speed of reaction, and they agree with the others given above. The conclusions which bear on our work on the urazoles was summed up as follows:

The speed of esterification is diversely influenced by substituting groups or elements of different relative mass. Symmetrical trisubstituted carboxylic acids are not esterified unless the carboxyl group is joined by one or more carbon atoms to the benzene nucleus. Symmetrical trichlor-, tribrom-, and trinitro-, and 2,6-dibrombenzoic acid are not esterified; thymolic, 2,6-hydroxyphenylbenzoic, and mesitylenecarboxylic acids are esterified.

Heating causes an increased action in some cases. Those radicals which prevent a reaction at high temperatures have a much greater relative mass than those which hinder action at lower temperature.

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[1] Meyer and Sudborough: Ber. d. chem. Ges., **27**, 510, 1580, 3146. Meyer: *Ibid.*, **28**, 182, 1254, 2773, 3197; **29**, 830, 839, 1397. Z. physik. Chem., **24**, 219.

The groups OH, CH_3, and F in the two ortho positions retard the formation of ethereal salts, while Cl, Br, I, and NO_2 prevent it altogether.

When working with isomeric compounds, those containing substituting groups in the meta position are perhaps most readily acted upon, the para compounds nearly to the same extent as the meta, and the ortho compounds least. Results obtained by Kellas[1] agree with this last statement, as shown by the following table:

Table J.

	Relative velocity.					
Position.	Cl.	Br.	I.	NO_2.	CH_3.	OH.
Ortho	35.7	7.0	9.3	4.2	28.4	15.3
Meta	55.2	18.4	28.3	22.3	63.8	55.9
Para	53.1	17.2	26.8	22.3	71.0	51.3

The order of the reaction velocity for ortho acids is as follows: Benzoic, chlorbenzoic, toluic, brombenzoic, iodobenzoic, nitrobenzoic; but toluic comes before chlorbenzoic for the meta and para acids, and nitro before iodo for meta acids. Therefore the effect of the molecular weight is only comparable for analogous compounds. In hydrolysis the velocity is least for ortho acids.

Brussoff[2] worked with 2-normal potassium hydroxide and alkyl iodides in 96 per cent alcohol at 78°. The following table shows the relative maximum velocity of the evolution of the corresponding olefine.

Table K.

Iodide.	Relative maximum velocity.
Ethyl	1.66
Propyl	2.24
Isopropyl	2.86
n-Butyl	1.00
Isobutyl	2.84
Secondary butyl	5.06
Tertiary butyl	8.00

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[1] Z. physik. Chem., **24**, 221.

[2] *Ibid.*, **34**, 129.

(1) "This shows that the mechanism of the reaction is different from that of the preceding work. The work shows that the velocity of the formation of the olefine is greatest from the iodides, from the bromides it is less, and it is smallest from the chlorides."

(2) "A change of solution from ethyl to methyl alcohol, or a change of alkali from potassium hydroxide to sodium hydroxide, has little effect on the velocity of formation of the olefine."

(3) "The amount of olefine formed, as well as the velocity of its formation, depends but little upon the primary, secondary, or tertiary constitution of the carbon chain, but primarily upon the number of side chains and their proximity to the side chain containing the halogen atom."

Our work, then, on the action of various alkyl halides on the salts of urazoles shows that the same stereochemical relations are involved in these alkylation reactions as were discovered in the various reactions discussed above.

10. *Results Similar to those Described in the Urazole Work.*

(1) *The speed of reaction of sodium 1-phenyl-3-thiourazole on sodium monochloracetate* was studied, both in water solution and in 50 per cent alcohol solution. All solutions were 0.2 N and the temperature was 50°. The value of K_1 in water solution was 0.189, while in 50 per cent alcohol solution K_1 was 0.150. See Tables XXXVII. and XXXVIII. in the experimental part. The sodium chloracetate was made by titrating a boiling solution of sodium bicarbonate, 20 cc. N solution, with chloracetic acid in the presence of phenolphthalein. The solution was then made up to 100 cc.

(2) *The action of sodium thioacetate on ethyl iodide* was investigated. The solutions used were 0.2 N, and the temperature was 25°. The sodium thioacetate was made by titrating 20 cc. of N sodium hydroxide with a water solution of thioacetic acid until the red color of phenolphthalein disappeared. The solution was then made up to 100 cc. The value of K_1 was found to be 0.40. See Table XXXIX. in the experimental part.

(3) *Action of N potassium hydroxide upon N ethyl iodide.*—It was suspected that when the alkyl halides react with alkali hydroxides, the reaction is really between the molecular alkyl halide and the hydroxyl ions. The following equation was found to express approximately the course of the reaction:

$$\frac{dx}{dt} = K_{trans}\,\alpha(A - x)(A - x) = K(A - x)^2 \qquad (1).$$

K_{trans} is the velocity constant, α the percentage of dissociation of the potassium hydroxide, A the original concentration of both the alkyl halide and the potassium hydroxide, and x the change in concentration of these two substances in the time t. If equation (1) expresses the reaction it is evident that the addition of potassium iodide should lower the value of α, and hence of K_1, *unless the potassium iodide has a large positive catalyzing effect.* In our work, since the data are lacking, α was assumed to be the same in 50 per cent alcohol as in water, and the formation of potassium alcoholate was left out of account. Since the potassium hydroxide and potassium alcoholate both react with the alkyl halide in independent side reaction, and since α is used only for comparison, the error involved in the assumptions is not large, but can well account for the difference between the theoretical and observed values of K_1.

AK in Table XL. was found to be 0.011, while in the presence of 5 molecular portions of potassium iodide the value of AK was lowered to 0.00614 instead of the calculated value 0.0082. The values of μ_v in 0.5 N and 3 N solutions were assumed to be 184 and 137.

The N potassium hydroxide solution was made by neutralizing barium hydroxide with potassium sulphate. The resulting solution was evaporated to a small volume in platinum dishes. The carbonate formed during evaporation was precipitated with barium hydroxide and the solution was then made normal by titrating it against N sulphuric acid and diluting it properly. K_1 was found to be 0.022. When the action was suppressed with 5 molecular portions of potassium iodide K_1 was lowered to 0.0123. See Tables XL. and XLI. in the experimental part.

(4) *Action of N potassium hydroxide upon N methyl iodide.* K_1 was found to be 0.178. When suppressed as before, K_1 was 0.085. The value of K_1 fell with considerable regularity, due to hydrolysis of the methyl iodide in 50 per cent alcoholic solution. To study the velocity of this hydrolysis a 0.5 N solution in 50 per cent alcohol, which has the same concentration as the reaction mixture above, was made and the velocity of the reaction was then determined as usual. The value of the concentration of the water hardly changes, and the methyl iodide is the only substance appreciably diminishing in concentration. The hydrolysis of the methyl iodide should follow approximately the equation for a reaction of the first order during the first part of the reaction, before the reverse reaction is appreciable. K was found to be 0.00023. See Tables XLII., XLIII., and XLIV., in the experimental part.

The reactions between potassium hydroxide and alkyl halides furnish excellent proof that, just as with the urazoles, the hydroxyl anion reacts with the molecular alkyl halide.

$$\overline{O}H + C_2H_5I \rightleftarrows C_2H_5\overline{I}.OH \rightarrow \overline{I} + C_2H_5OH.$$

EXPERIMENTAL.

The 1-phenyl-3-thiourazole was prepared according to the method described by Acree.[1] The ethyl 1-phenylthiosemicarbazide-1-carboxylate was purified by extraction in a Soxhlet apparatus with alcohol, and crystallization. It melted at 221°. By this method a pure 1-phenyl-3-thiourazole, m. p. 192°–193°, was obtained.

The sodium 1-phenyl-3-thiourazole was made by weighing out a quantity of the phenyl-3-thiourazole and titrating this with the theoretical amount of purified and dried sodium bicarbonate in solution. The solution was evaporated to dryness, heated to constant weight, and placed in a desiccator. To make solutions of the required normality from this salt, the theoretical weight was dissolved in water and diluted to the required volume. The alkyl halides were made by Kahlbaum and were redistilled before use.

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[1] Ber. d. chem. Ges., **36**, 3151.

Unless otherwise stated, all alkyl halide solutions were made in absolute alcohol as follows: A measuring flask was nearly filled with absolute alcohol and weighed. Then a slight excess of the alkyl halide (the volume was calculated from its specific gravity) was measured into the flask, which was then weighed a second time. The flask was then kept in the thermostat until a temperature of 25° was reached, and it was then filled to the mark. The amount of absolute alcohol necessary to dilute the alkyl halide solution to the proper strength was then added. These solutions of sodium salt and alkyl halide were kept in a bath at 25°. Ten cc. portions of each were then measured into test tubes by means of carefully graduated pipettes; the concentrations at the top of each table in the experimental part refer to the separate solutions before they were mixed. The urazole solution was measured in first, because the evaporation from the water solution was slight. Then the solution of alkyl halide was added, the point of the pipette being kept below the liquid in the test tube to prevent evaporation. The test tubes were then tightly corked, and, after various time intervals, were quickly poured into 200 cc. of water, containing 4 cc. of starch solution. This resulting solution was then quickly titrated with a standard iodine solution. The alkylation reaction was, of course, nearly stopped by the large dilution with water.

The bath was the one used in the conductivity measurements. The water was kept well stirred with a water motor and propeller and the temperature was carefully regulated.

The error in titration was slight, as it was found that sodium 1-phenyl-3-thiourazole titrates with iodine as sharply as does a thiosulphate.

The error due to the hydrolysis or decomposition of the alkyl halide in the water solution was noticeable. This tended to reduce the speed of the alkylation and so lowered the constant. See Table XLIV., and also the note to Table XL.

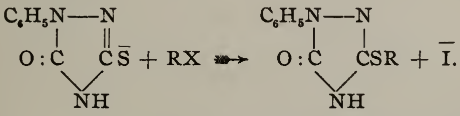
A third error was introduced by the formation of 1-phenyl-3-thiourazole through the hydrolysis of the sodium 1-phenyl-

3-thiourazole by water. The phenyl-3-thiourazole is more slowly alkylated than the sodium salt. This tends to lower the constant.

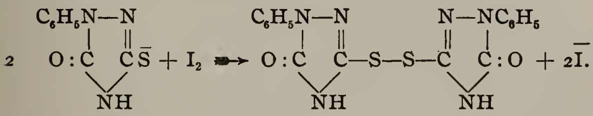
A fourth error could arise from the reaction of the sodium hydroxide, formed by the hydrolysis of the sodium phenyl-3-thiourazole, with the alkyl halide. By this reaction the concentration of the alkyl halide, and consequently the value of the constant, is lowered.

The error due to the volatilization of the alkyl halide was carefully guarded against, but must be appreciable. Rubber stoppers were used in the test tubes when the experiments were performed at 50°.

The reaction of the alkyl halides on the sodium thiourazole proceeds as follows:



The action of iodine on the sodium 1-phenyl-3-thiourazole is the following:



In obtaining the data for the following tables all of the values are expressed in terms of cc. of standard iodine solution; these are directly proportional to cc. of standard solution, and therefore weights, of sodium 1-phenyl-3-thiourazole (or acid). *A* is the original amount of sodium 1-phenylthiourazole taken for each titration, *x* is the amount changed in time *t*, and *A*—*x* is the unchanged urazole salt (or acid). We assumed that the alkyl halides react only with the ions of the sodium 1-phenyl-3-thiourazole (or acid), and are not appreciably hydrolyzed or decomposed. Then *A*, *x*, and *A*—*x* can also represent the corresponding values of the alkyl halides. t is expressed in minutes.

The values for the amounts of the phenylalkylthiourazole formed could also be used. A could be calculated theoretically from the original concentration of sodium 1-phenyl-3-thiourazole, or the alkyl derivative formed could be separated and weighed after each experiment is complete. Both of these methods have been used in previous work by Acree,[1] Brunel, and Johnson. A and x would then represent the amount of phenylalkylthiourazole formed after time t.

The values of A_1K_1 and K_1 given with each table are calculated on the basis that A is some multiple of 10 cc., and K_1 is the value of the velocity constant when the concentration is 1 gram molecule per liter. K_1 should be, and is, nearly independent of the concentration because the percentage of ionization of the salt changes very little with the change in concentration employed in these experiments. The solvent was 50 per cent alcohol unless otherwise stated. The concentrations given at the head of each table are those of the individual solutions before they were mixed.

Table I.

25°. 0.1 N sodium 1-phenyl-3-thiourazole +0.1 N C_2H_5I.

t.	A.	$A-x$.	x.	AK.
35	10.95	6.81	4.14	0.0174
60	10.95	5.42	5.53	0.0170
120	10.95	3.58	7.37	0.0172
240	10.95	2.20	8.75	0.0166
			Average,	0.0173

$A_1K_1 = 0.0158$ and $K_1 = 0.316$

The effect of various organic and inorganic substances on the velocity constant of the reaction between 0.1 N sodium 1-phenyl-3-thiourazole and 0.1 N C_2H_5I was studied.

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[1] This Journal, 37, 71.

Table II.

t.	A.	A—x.	x.	AK.			
120	10.95	3.80	7.15	0.0156	3 mols	NaCl	(0.1754 grams)
120[1]	10.95	4.11	6.84	0.0138	3 "	$NaNO_3$	(0.2551 ")
120[2]	10.86	4.50	6.37	0.0118	3 "	KNO_3	(0.3035 ")
120	10.86	4.80	7.06	0.0154	3 "	Na_2SO_4	(0.4262 ")
120	10.86	3.70	7.16	0.0161	3 "	$NaI.2H_2O$	(0.5516 ")
120	10.86	4.00	6.86	0.0150	10 "	NaI	(1.4986 ")
120	10.86	4.26	6.62	0.0130	15 "	NaI	(2.2479 ")
120	10.86	4.96	6.90	0.0145	15 "	KBr	(1.7866 ")
120	10.86	3.98	6.88	0.0144	15 "	NaBr	(1.5445 ")
120	10.86	4.27	6.58	0.0128	15 "	$BaCl_2.2H_2O$	(3.3947 ")
120	10.86	3.36	7.50	0.0186	20 "	urea	(1.2012 ")
120	10.86	3.54	7.32	0.01715	10 "	cane sugar	(3.4218 ")
+120	10.86	3.54	7.32	0.01715	10 "	" "	(3.4218 ")
120	10.86	3.38	7.48	0.0184	15 "	glucose	(2.7014 ")
120	10.86	3.35	7.51	0.0186	10 "	mannite	(1.8211 ")

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[1] The very great suppression caused by sodium nitrate and potassium nitrate may be explained by assuming that these salts react with ethyl iodide and form ethyl nitrate. This, in turn, may be hydrolyzed and form nitric acid or may react with sodium 1-phenyl-3-thiourazole and give 1-phenyl-3-ethylthiourazole. This nitric acid would react with the sodium 1-phenyl-3-thiourazole and form phenyl-3-thiourazole, which would be alkylated much more slowly than the sodium 1-phenyl-3-thiourazole. All of these changes would tend to aid the suppression of the value of the constant.

[2] This experiment was repeated and gave identical results.

Table III.

25°. 0.05 N Sodium 1-phenyl-3-thiourazole +0.05 N C_2H_5I

t.	A.	$A-x$.	x.	AK.
30	4.72	3.65	1.07	0.00977
60	4.72	3.02	1.70	0.00938
180	4.72	1.795	2.925	0.00905
310	4.72	1.09	3.63	0.00922

Average, 0.00935

$A_1K_1 = 0.00991$ and $K_1 = 0.396$

Table IV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole +0.2 N C_2H_5I.

t.	A.	$A-x$.	x.	AK.
15	18.88	12.29	6.59	0.0357
32	18.88	8.90	9.98	0.0350
60	18.88	6.00	12.88	0.0357
120	18.88	3.43	15.45	0.0375

Average, 0.0359

$A_1K_1 = 0.0361$ and $K_1 = 0.361$

Table V.

25°. 0.4 N Sodium 1-phenyl-3-thiourazole +0.4 N C_2H_5I.

t.	A.	$A-x$.	x.	AK.
15	37.76	19.00	18.76	0.0658
30	37.76	12.80	24.96	0.0650
45	37.76	9.47	28.29	0.0663
60	37.76	7.20	30.475	0.0697

Average, 0.0667

$A_1K_1 = 0.0706$ and $K_1 = 0.352$

The average value for K_1 in Tables I., III., IV., and V. is 0.36.

Table VI.

50°. 0.1 N Sodium 1-phenyl-3-thiourazole +0.1 N C_2H_5I.

t.	A.	$A-x$.	x.	AK.
10	9.44	3.80	5.64	0.148
20	9.44	2.26	7.18	0.159
40	9.44	1.30	8.14	0.156
81	9.44	0.70	8.74	0.154
190	9.44	0.30	9.14	0.160

Average, 0.155

$A_1K_1 = 0.164$ and $K_1 = 3.28$

Table VII.

0°. 0.1 N Sodium 1-phenyl-3-thiourazole+0.1 N C_2H_5I.

t.	A.	A—x.	x.	AK.
30	10.86	10.03	0.83	(0.00275)
60	10.86	9.70	1.16	0.00191
120	10.86	9.06	1.80	0.00168
563	10.86	6.09	4.77	0.00139
1080	10.86	4.28	6.58	0.00142
			Average,	0.00160

A_1K_1 = 0.00147 and K_1 = 0.029

Table VIII.

25°. 0.2 N Barium 1-phenyl-3-thiourazole+0.2 N C_2H_5I.

t.	A.	A—x.	x.	AK.
15	19.80	13.55	6.25	0.0307
30	19.80	10.00	9.80	0.0326
60	19.80	6.86	12.94	0.0316
120	19.80	4.10	15.70	0.0319
			Average,	0.0317

A_1K_1 = 0.032 and K_1 = 0.32

15 mols. $BaCl_2.2H_2O$ (6.4070 grams) added.

128	19.80	7.25	12.55	0.0135

After standing two days in the cold and one day at 75° only half a drop of iodine was required for the titration, so the reaction was complete.

Table IX.

25°. 0.2 N Magnesium 1-phenyl-3-thiourazole+0.2 N C_2H_5I.

t.	A.	A—x.	x.	AK.
15	16.908	11.15	5.758	0.0344
30	16.908	8.14	8.768	0.0359
60	16.908	5.20	11.708	0.0375
120	16.908	2.70	14.208	(0.0438)
			Average,	0.0359

A_1K_1 = 0.0425 and K_1=0.425

Table X.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole +0.1 N CH_3I.

t.	*A.*	*A—x.*	*x.*	*AK.*
5	10.86	3.50	7.36	0.420
10	10.86	2.30	8.56	0.371
20	10.86	1.33	9.53	0.358
30	10.86	0.78	10.08	0.416
60	10.86	0.56	10.30	(0.306)
120	10.86	0.67	10.19	(0.126)

Average, 0.391

$A_1K_1 = 0.360$ and $K_1 = 7.20$

5 mols. NaI (0.7493 gram) added.

120	10.86	2.81	8.05	0.0238

Table XI.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole +0.1 N *n*-propyl iodide.

t.	*A.*	*A—x.*	*x.*	*AK.*
30	10.86	8.09	2.77	0.0114
60	10.86	6.60	4.26	0.0107
120	10.86	4.70	6.10	0.0107
240	10.86	3.00	7.86	0.0109

Average, 0.0109

$A_1K_1 = 0.010$ and $K_1 = 0.20$

5 mols. NaI (0.7493 gram) added.

120	10.86	5.19	5.67	0.0091

Table XII.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole +0.1 N isopropyl iodide.

t.	*A.*	*A—x.*	*x.*	*AK.*
30	10.86	10.24	0.62	(0.00203)
60	10.86	10.07	0.79	0.00137
120	10.86	9.54	1.32	0.00115
240	10.86	8.60	2.26	0.00109

Average, 0.0012

$A_1K_1 = 0.0011$ and $K_1 = 0.022$

5 mols. NaI (0.7493 gram) added.

120	10.86	9.70	1.16	0.000997

Table XIII.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N *n*-butyl iodide.

t.	*A.*	*A—x.*	*x.*	*A K.*
30	10.86	7.95	2.91	0.0122
60	10.86	6.50	4.36	0.0112
120	10.86	4.565	6.295	0.0115
240	10.86	2.90	7.96	0.0114
			Average,	0.0116

$A_1K_1 = 0.0107$ and $K_1 = 0.214$

Table XIV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isobutyl iodide.

t.	*A.*	*A—x.*	*x.*	*A K.*
240	19.00	15.30	3.70	0.001004
480	19.00	13.57	5.43	0.000833
1320	19.00	9.78	9.22	0.000714
			Average,	0.00080

$A_1K_1 = 0.00085$ and $K_1 = 0.0085$

Table XV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N ter. butyl iodide.

t.	*A.*	*A—x.*	*x.*	*A K.*
30	21.76	21.14	0.62	(0.000977)
240	19.00	18.40	0.60	0.000136
480	19.00	18.30	0.70	0.0000795
1320	19.00	18.11	0.89	0.0000372
			Average,	0.0000842

$A_1K_1 = 0.0000886$ and $K_1 = 0.00088$

Table XVI.

For this table and the three following this formula was used: $(A - B)K = \frac{1}{t} \log \frac{B(A - x)}{A(B - x)}$.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.066 N *n*-hexyl iodide.

t.	A.	$A - x$.	x.	$B - x$.	B.	$(A - B)K$.
30	19.00	18.49	0.51	5.82	6.33	(0.000822)
240	19.00	16.59	2.41	3.92	6.33	0.000621
420	19.00	15.60	3.40	2.93	6.33	0.000592
1320	19.00	13.43	5.57	0.76	6.33	0.000582

Average, 0.000601
$(A_1 - B_1)K_1 = 0.00063$
and $K_1 = 0.0095$

Table XVII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.066 N *n*-octyl iodide.

t.	A.	$A - x$.	x.	$B - x$.	B.	$(A - B)K$.
30	19.00	18.08	0.92	5.41	6.33	(0.00135)
240	19.00	15.70	3.30	3.03	6.33	0.000987
420	19.00	14.54	4.46	1.87	6.33	0.000983
1320	19.00	12.90	6.10	0.23	6.33	(0.000201)

Average, 0.000985
$(A_1 - B_1)\ K_1 = 0.00103$
and $K_1 = 0.16$

Table XVIII.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.033 N *n*-cetyl iodide.

t.	A.	$A - x$.	x.	$B - x$.	B.	$(A - B)K$.
120	9.50	9.37	0.13	3.036	3.166	0.0000193
240	9.50	9.27	0.23	2.936	3.166	0.0000508
480	9.50	9.06	0.44	2.726	3.166	0.0000718
1500	9.50	9.02	0.48	2.680	3.166	0.0000259

Average, 0.0000419
$(A_1 - B_1)\ K_1 = 0.0000441$
and $K_1 = 0.00132$

Table XIX.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.05 N isoamyl iodide.

t.	*A.*	*A—x.*	*x.*	*B—x.*	*B.*	*(A—B)K.*
120	9.50	7.32	2.18	2.57	4.75	0.00128
240	9.50	6.44	3.06	1.69	4.75	0.00117
480	9.50	5.67	3.83	0.92	4.75	0.00102
1500	9.50	4.84	4.66	0.09	4.75	0.000953

Average, 0.0011

$(A_1—B_1)\ K_1 = 0.00116$

and $K_1 = 0.046$

Table XX.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N ethyl bromide.

t.	*A.*	*A—x.*	*x.*	*A K.*
30	19.22	14.28	4.94	0.01153
60	19.22	11.60	7.62	0.01095
120	19.22	8.10	11.12	0.01144
240	19.22	5.24	13.98	0.01111

Average, 0.01126

$A_1K_1 = 0.0117$ and $K_1 = 0.117$

15 mols. NaBr (1.5445 grams) added.

120	19.22	9.30	9.92	0.00888

Table XXI.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-propyl bromide.

t.	*A.*	*A—x.*	*x.*	*A K.*
30	19.22	15.52	3.70	0.00761
60	19.22	13.48	5.74	0.00709
120	19.22	10.30	8.92	0.00721
240	19.22	6.89	12.33	0.00745

Average, 0.00734

$A_1K_1 = 0.00764$ and $K_1 = 0.076$

Table XXII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isopropyl bromide.

t.	A.	A—x.	x.	AK.
30	19.22	18.68	0.54	(0.000963)
120	19.22	17.84	1.38	0.000644
240	19.22	16.82	2.40	0.000594
420	19.22	15.52	3 70	0.000568
			Average,	0.000602

A_1K_1 = 0.000626 and K_1 = 0.0063

Table XXIII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-butyl bromide.

t.	A.	A—x.	x.	AK.
60	19.10	13.22	5.88	0.00741
120	19.10	10.07	9.03	0.00747
'240	19.10	7.10	12.00	0.00704
360	19.10	5.50	13.60	0.00687
480	19.10	4.53	14.57	0.00670
			Average,	0.0071

A_1K_1 = 0.00743 and K_1 = 0.074

Table XXIV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isobutyl bromide.

t.	A.	A—x.	x.	AK.
120	19.10	17.50	1.60	0.000761
240	19.10	16.40	2.70	0.000687
480	19.10	15.31	3.79	0.000516
660	19.10	14.52	4.59	0.000480
			Average,	0.000611

A_1K_1 = 0.000640 and K_1 = 0.0064

Table XXV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N ter. butyl bromide.

t.	*A.*	*A—x.*	*x.*	*AK.*
120	19.10	18.80	0.30	0.000132
240	19.10	18.70	0.80	0.000182
480	19.10	18.63	0.47	0.0000525
660	19.10	18.45	0.65	0.0000534
			Average,	0.000105

$A_1K_1 = 0.000110$ and $K_1 = 0.0011$

Table XXVI.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isoamyl bromide.

t.	*A.*	*A—x.*	*x.*	*AK.*
30	19.22	17.43	1.79	0.00342
70	19.22	15.46	3.76	0.00347
120	19.22	13.74	5.48	0.00333
240	19.22	10.54	8.68	0.00343
			Average,	0.00342

$A_1K_1 = 0.00356$ and $K_1 = 0.0356$

Table XXVII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-propyl chloride.

t.	*A.*	*A—x.*	*x.*	*AK.*
60	18.88	18.58	0.30	(0.000269)
240	18.88	18.30	0.58	0.000132
660	18.88	17.45	1.43	0.000128
1440	18.88	16.30	2.58	0.000110
			Average,	0.00012

$A_1K_1 = 0.00013$ and $K_1 = 0.0013$

15 mols. NaCl (0.8769 gram) added.

660	18.88	17.75	1.13	0.0000965

Table XXVIII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isopropyl chloride.

t.	A.	$A - x$.	x.	AK.
120	18.88	18.58	0.30	0.000134
480	18.88	18.40	0.48	0.0000543
720	18.88	18.40	0.48	0.0000362
1440	18.88	18.33	0.55	(0.0000206)

Average, 0.0000748

$A_1K_1 = 0.00008$ and $K_1 = 0.0008$

Table XXIX.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-butyl chloride.

t.	A.	$A - x$.	x.	AK.
120	18.58	17.48	1.10	0.000524
240	18.58	17.39	1.19	0.000283
480	18.58	16.87	1.71	0.000211
1440	18.58	15.74	2.84	(0.000125)

Average, 0.000340

$A_1K_1 = 0.000365$ and $K_1 = 0.0036$

Table XXX.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isobutyl chloride.

t.	A.	$A - x$.	x.	AK.
120	18.88	18.66	0.22	(0.0000982)
440	18.88	18.58	0.30	0.0000336
720	18.88	18.58	0.30	0.0000224
1440	18.88	18.15	0.73	0.0000279

Average, 0.000028

$A_1K_1 = 0.0000295$ and $K_1 = 0.00029$

Table XXXI.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N tertiary butyl chloride.

.t	A.	A—x.	x.	AK.
120	18.88	18.27	0.61	(0.000277)
480	18.88	18.29	0.59	0.0000672
720	18.88	18.19	0.68	0.0000591
1440	18.88	18.06	0.82	0.0000308

Average, 0.000052

$A_1K_1 = 0.000055$ and $K_1 = 0.00055$

Table XXXII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isoamyl chloride.

t.	A.	A—x.	x.	AK.
60	18.88	18.60	0.28	(0.000250)
240	18.88	18.49	0.39	0.0000870
660	18.88	18.10	0.78	0.0000653
1440	18.88	17.40	1.48	(0.0000591)

Average, 0.000071

$A_1K_1 = 0.000075$ and $K_1 = 0.00075$

Table XXXIII.

50°. 0.05 N 1-Phenyl-3-thiourazole + 0.05 N ethyl iodide.

t.	A.	A—x.	x.	AK.	K_1.
5	4.90	4.11	0.79	0.0384	
				$A_1K_1=0.0392$	1.568
10	4.90	3.57	1.33	0.0373	
				$A_1K_1=0.0380$	1.520
15	4.90	3.18	1.72	0.0360	
				$A_1K_1=0.0367$	1.468
31	4.90	2.46	2.44	0.0319	
				$A_1K_1=0.0325$	1.300
60	4.90	1.88	3.02	0.0268	
				$A_1K_1=0.0273$	1.096
120	4.90	1.29	3.61	0.0234	
				$A_1K_1=0.0238$	0.952
240	4.90	0.66	4.24	0.0268	
				$A_1K_1=0.0273$	1.096
5 mols. HCl. (sp. gr. 1.20)(0.388 cc.) added.					
60	4.71	3.54	1.17	0.0055	

Table XXXIV.

50°. 0.05 N 1-Phenyl-3-thiourazole + 0.05 N methyl iodide.

t.	A.	$A-x$.	x.	AK.	K_1.
3	4.90	2.05	2.85	0.463	
				$A_1K_1=0.472$	18.88
5	4.90	1.40	3.50	0.500	
				$A_1K_1=0.510$	20.40
10	4.90	0.90	4.20	0.444	
				$A_1K_1=0.453$	18.12
15	4.90	0.75	4.15	0.369	
				$A_1K_1=0.377$	15.04
30	4.90	0.67	4.23	0.210	
				$A_1K_1=0.214$	8.56
60	4.90	0.93	3.97	0.0711	
				$A_1K_1=0.0725$	2.90

Table XXXV.

25°. 0.05 N 1-Phenyl-3-thiourazole + 0.05 N ethyl iodide.

t.	A.	$A-x$.	x.	AK.
60	4.71	3.69	1.02	0.00460
150	4.71	2.83	1.88	0.00443
			Average,	0.00451

$A_1K_1 = 0.00479$ and $K_1 = 0.192$

Table XXXVI.

Change of 1-Phenyl-3-thiourazole into the Disulphide.

50°. 0.05 N 1-Phenyl-3-thiourazole in 50 per cent alcohol.

t.	A.	$A-x$.	x.	AK.
61	4.90	4.87	0.03	0.000101
150	4.90	4.82	0.08	0.000110
214	4.90	4.78	0.12	0.000116
300	4.90	4.68	0.22	0.0001085
390	4.90	4.64	0.26	0.000143
			Average,	0.00012

$A_1K_1 = 0.00012$ and $K_1 = 0.0024$

Table XXXVII.

50°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N sodium chloracetate in water solution.

t.	*A.*	*A—x.*	*x.*	*A K.*
15	18.50	15.60	2.90	(0.0124)
30	18.50	12.00	6.50	0.0180
60	18.50	8.97	9.53	0.0177
120	18.50	6.14	12.36	0.0168
			Average,	0.0175

A_1K_1 = 0.0189 and K_1 = 0.189

Table XXXVIII.

50°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N sodium chloracetate in 50 per cent alcohol.

t.	*A.*	*A—x.*	*x.*	*A K.*
15	18.71	15.30	3.41	0.0148
30	18.71	13.13	5.58	0.0141
60	18.71	10.39	8.32	0.0133
			Average,	0.0141

A_1K_1 = 0.015 and K_1 = 0.15

Table XXXIX.

25°. 0.2 N Sodium thioacetate + 0.2 N ethyl iodide.

t.	*A.*	*A—x.*	*x.*	*A K.*
15	13.78	10.20	3.78	0.0252
30	13.78	7.41	6.37	0.0286
60	13.78	5.02	8.76	0.0290
120	13.78	2.54	11.24	(0.0368)
240	13.78	0.90	12.88	(0.0596)
			Average,	0.027

A_1K_1 = 0.040 and K_1 = 0.40

Table XL.

50°. N Potassium hydroxide + N ethyl iodide.

t.	*A.*	*A—x.*	*x.*	*A K.*
15	10.00	8.47	1.53	0.0120
30	10.00	7.49	2.51	0.0111
60	10.00	6.18	3.82	0.0103
120	10.00	4.37	5.63	0.0107
			Average,	0.011

K_1 = 0.022

After the normal ethyl iodide in absolute alcohol had stood for forty-eight hours, 10 cc. were titrated with 0.1 N potassium hydroxide. 4.56 cc. were required. This showed that the ethyl iodide may be decomposed in the water and alcohol and accounts for the decrease in the velocity constant in the above table. See also Table XLIV.

Table XLI.

50°. N Potassium hydroxide and N ethyl iodide with 5 mols. KI (8.30 grams) added.

t.	*A.*	*A—x.*	*x.*	*A K.*
15	10.00	8.99	1.01	0.00741
30	10.00	8.37	1.63	0.00648
60	10.00	7.50	2.50	0.00555
120	10.00	6.19	3.81	0.00512

Average, 0.00614
K_1 = 0.01228

Table XLII.

50°. N Potassium hydroxide + N methyl iodide.

	A.	*A—x.*	*x.*	*AK.*
4	10.00	7.05	2.95	0.104
8	10.00	5.69	4.31	0.0947
15	10.00	4.39	5.61	0.0852
32	10.00	2.99	7.01	0.0733

Average, 0.0893
K_1 = 0.1786

Table XLIII.

50°. N Potassium hydroxide and N methyl iodide with 5 mols. KI (8.30 grams) added.

t.	*A.*	*A—x.*	*x.*	*A K.*
4	10.00	8.40	1.60	0.0476
8	10.00	7.19	2.81	0.0382
15	10.00	5.91	4.09	0.0461
32	10.00	4.50	5.50	0.0381

Average, 0.0425
K_1 = 0.085

Table XLIV.

50°. Hydrolysis 0.5 N methyl iodide in 50 per cent alcohol.

t.	A.	$A-x$.	$K=\frac{1}{t}\log\frac{A}{A-x}$.
4	9.83	9.81	0.00022
9	9.83	9.77	0.00029
32	9.87	9.66	0.00024
90	9.87	9.42	0.00020
180	9.83	9.30	(0.00012)
240	9.83	8.67	0.00022
1440	9.83	6.51	(0.00012)
		Average,	0.00023

Table XLV.

The reaction between sodium phenyl-3-thiourazole and ethyl iodide was followed by means of conductivity measurements. Special experiments showed that the conductivity of the sodium urazole was not changed by the addition of the ethyl iodide. This shows that the ethyl iodide does not unite appreciably with the sodium or urazole ions.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N C_2H_5I in 50 per cent ethyl alcohol.

μv.	t.	Resistance.	a.	b.	AK.
15.48	0.0	102	54.70	45.30	....
16.52	2.9	102	56.30	43.70	0.0530
17.42	6.0	102	57.60	42.40	0.0728
17.90	11.3	60	45.10	54.90	0.0539
18.80	17.3	60	46.30	53.76	0.0620
19.95	30.2	60	47.80	52.20	0.0972
21.02	56.2	60	49.10	50.90	0.114
21.46	77.5	60	49.60	50.40	0.155
21.88	....	60	50.10	49.90	

It is evident that the method must be studied further in order to secure better constants. The conductivity data prove conclusively that only a very small amount of alkyl halide can be combined at any moment with the sodium or urazole ions.

Table XLVI.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N C_2H_5I in 50 per cent ethyl alcohol.

$\mu v.$	$t.$	Resistance.	$a.$	$b.$	$AK.$
17.62	0.0	140	48.10	51.90	......
18.79	4.8	140	49.70	50.30	0.0309
20.52	13.3	140	51.90	48.10	0.0356
21.88	24.5	140	53.50	46.50	0.0366
22.87	31.6	140	54.60	45.40	0.0442
23.72	44.6	140	55.50	44.50	0.0470
24.30	59.6	140	56.10	43.90	0.0482
24.78	77.8	100	48.20	51.80	0.0496
26.63	....	100	50.00	50.00	......

The method must be improved by further work.

Conclusions.

1. Work on the reactions of alkyl halides with urazoles, hydroxides, carbonates, thioacetates, etc., seems to prove that the alkyl halide reacts with the anion of the urazole, hydroxide, etc., according to the expression

$$C_2H_5I + \overset{-}{\mathrm{OH}} \rightarrow C_2H_5OH + \overset{-}{\mathrm{I}},$$

or

$$\frac{dx}{dt} = K_{trans} \times C_{ethyl\ iodide} \times C_{OH}.$$

2. The alkyl halides do not seem to form alkyl derivatives of other substances through the intermediate dissociation into alkyl and halide ions, as Bruyn and Steger assumed:

$$\mathrm{KOH} + C_2H_5I \rightleftarrows \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{OH}} + \overset{+}{C_2H_5} + \overset{-}{\mathrm{I}} \rightarrow C_2H_5OH + \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{I}}.$$

3. The experimental evidence is not in harmony with the view of Nef that alkyl halides react with compounds because the alkyl halide first dissociates into the corresponding halogen acid and an unsaturated methylene or olefine derivative, which then reacts with another substance:

$$\begin{aligned} &C_2H_5I + \overset{+}{\mathrm{K}} + \overset{-}{OC_2H_5} \rightleftarrows \\ &\qquad CH_3CH{\scriptstyle\rightarrow\atop\rightarrow} + \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{I}} + \overset{+}{\mathrm{K}} + \overset{-}{OC_2H_5} \rightarrow \\ &\qquad\qquad CH_3CH{\scriptstyle\rightarrow\atop\rightarrow} + HOC_2H_5 + \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{I}} \rightarrow \\ &\qquad\qquad\qquad CH_3CH_2{-}O{-}C_2H_5 + \overset{+}{\mathrm{K}} + \overset{-}{\mathrm{I}}. \end{aligned}$$

see errata
p. 823

4. The alkyl halides do not seem to react with salts by first uniting with the cation and forming a complex cation which then reacts with the anion, as Euler assumed:

$$C_2H_5I + \overset{+}{K} + \overset{-}{OH} \rightleftarrows C_2H_5I.\overset{+}{K} + \overset{-}{OH} \rightarrow$$
$$C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

5. The alkyl halide seems to react as a neutral molecule with the anion of the substance which is alkylated, perhaps forming an unstable intermediate complex anion.

6. The alkyl iodides are more reactive towards the urazoles than are the alkyl bromides, and these in turn are more reactive than the alkyl chlorides. The primary alkyl halides are more reactive towards the urazoles than are the secondary alkyl halides, and these are more reactive than the tertiary alkyl halides. The so-called space interference seems to be effective in these reactions.

JOHNS HOPKINS UNIVERSITY,
June 1, 1907.

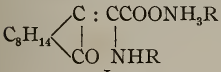
STUDY OF THE ACTION OF PRIMARY AND TERTIARY AMINES ON CAMPHOROXALIC ACID.

[XII. COMMUNICATION ON CAMPHOROXALIC ACID.[1]]

BY J. BISHOP TINGLE AND L. F. WILLIAMS.

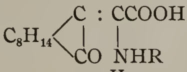
THEORETICAL.

In a series of papers by J. Bishop Tingle and his coworkers it has been shown that camphoroxalic acid combines with a number of primary amines to form condensation products which usually belong to the three types,



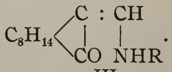
$$C_8H_{14}\left\langle\begin{array}{ll}C & :\ CCOONH_3R\\ | & \quad |\\ CO & \quad NHR\end{array}\right.$$

I.



$$C_8H_{14}\left\langle\begin{array}{ll}C & :\ CCOOH\\ | & \quad |\\ CO & \quad NHR\end{array}\right.$$

II.



$$C_8H_{14}\left\langle\begin{array}{ll}C & :\ CH\\ | & \quad |\\ CO & \quad NHR\end{array}\right. .$$

III.

In the case of some amines which contain more than one amino group, such as benzidine,[2] the compound, though apparently different from the above typical forms, is probably fundamentally similar, one amino group condensing and one neutralizing the carboxyl, as expressed by the formula

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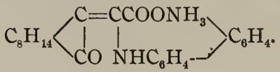
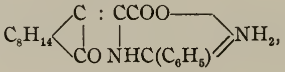
[1] The other papers relating to this subject have been published as follows: Inaug. Dissn., Munich, 1889, p. 34; J. Chem. Soc., **57**, 652 (1890); THIS JOURNAL, **19**, 393 (1897); **20**, 318 (1898); **21**, 238 (1899); **23**, 214 (1900); J. Am. Chem. Soc., **23**, 363 (1901). THIS JOURNAL, **34**, 217 (1905); **36**, 223 (1906); J. Am. Chem. Soc., **29**, 1242 (1907); THIS JOURNAL, **39**, 105 (1908).

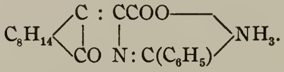
[2] THIS JOURNAL, **34**, 231 (1905).



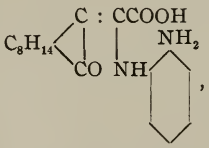
The product formed with benzamidine[1] is probably essentially similar in constitution,



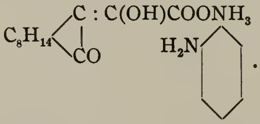
or



In the case of orthophenylenediamine[2] another complication is encountered. It is evident that a compound of type II,



would be extremely likely to combine further to form a five-membered ring, and that the same would, of course, be true if the amino group first attacked the carboxyl, as in the case of a substance with the structure



Experiment showed that this actually took place because, in spite of many attempts to do so, it was not found to be possible to isolate any compound corresponding to either of the two formulae given above, or to such a substance as is represented by the expression

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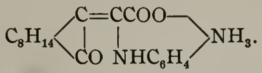
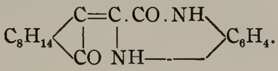
[1] This Journal, **34**, 230 (1905).

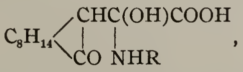
[2] J. Amer. Chem. Soc., **23**, 375 (1901).



The compound which was actually obtained, as the result of a number of experiments carried out under very varied conditions, was the quinoxaline derivative,



The formation, primarily, in all these cases, of an addition compound,



is, of course, assumed. A number of such additive products from primary amines have been definitely isolated and studied by the senior author, alone, and in conjunction with Alfred Tingle, W. E. Hoffman, Jr., and C. J. Robinson.[1]

Their constitution and the bearing which their formation has on the ketonic-enolic question have been fully considered and discussed.[2] A number of addition compounds of camphoroxalic acid and secondary amines have been described by Bishop Tingle and W. E. Hoffman, Jr.,[3] and also by the present authors.[4]

Returning, now, to the substances belonging to the three types formulated above, there are two points which call for comment. A given amine is not necessarily capable of forming compounds belonging to each of these classes; some can do so, others only yield two, and certain amines appear to be able to give not more than one of them; in this latter event it is usually the substance belonging to type three which is formed. We shall return to this point after presenting our own results.

[1] *Loc. cit.*

[2] *Vide*, especially, This Journal, **36**, 223 (1906).

[3] *Ibid.*, **34**, 217 (1905).

[4] *Ibid.*, **39**, 122 (1908). Cf. O. Dimroth: Ber. d. chem. Ges., **40**, 2404 (1907).

An inspection of the amines hitherto employed for the condensations discloses the fact that a considerable number have failed to react at all with camphoroxalic acid. It is obvious that the cause of this failure must be cleared up before it will be possible to formulate the regularity underlying the reactions in question. Further, it is desirable to increase the available data by extending the experiments so as to include a larger number of amines within the scope of the investigation. This was, therefore, our first object in undertaking the investigation whose results are recorded in the present paper.

The readiness with which aniline reacts with camphoroxalic acid,[1] and the difficulty experienced in obtaining condensation products with paranitraniline, on the one hand, and with para- and metaphenylenediamine[2] on the other, made it desirable to investigate the behavior of the aminophenols in this connection, because these latter compounds might be regarded as being in a position midway between the substances in question. They are less basic than aniline, but more so than the nitranilines. They are disubstituted compounds like the nitranilines and phenylenediamines, but, in the case of the aminophenols, a condensation, in addition to salt formation, is highly improbable. This latter point is of some importance, because it has been shown by Bishop Tingle, in conjunction, with Messrs. Cram[3] and Lovelace,[4] that salt formation is, in some cases, an important factor in promoting intramolecular condensations.

The objection might be raised that there is nothing to prevent the aminophenols from first forming salts which could afterwards undergo rearrangement and condensation. The answer to this is found in the work of Bishop Tingle and Alfred Tingle[5] on the compounds of aniline and camphoroxalic acid, and especially in their results with *o*-phenylenediamine. They found that this base gave the compound mentioned above, alike from the free acid, its sodium salt, or from ethyl camphoroxalate. The same point is demonstrated by our own results with benzalaniline and camphoroxalic acid, cf. p. 285.

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[1] This Journal, **21**, 238 (1899).

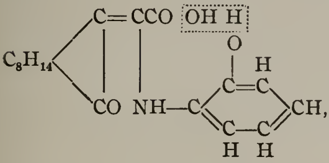
[2] *Ibid.*, **34**, 253 (1905).

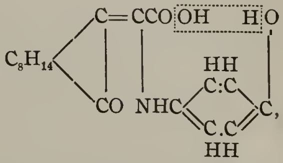
[3] *Ibid.*, **37**, 596 (1907).

[4] *Ibid.*, **38**, 642 (1907).

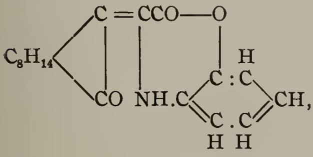
[5] *Loc. cit.*

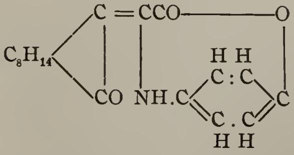
Assuming, then, that the amino groups of ortho- and par-aminophenol combine in the regular manner with camphor-oxalic acid, it is at least conceivable that the resulting substances,


, and


,

might eliminate the elements of water, as shown by the dotted lines in the preceding formulae or in some other manner, giving rise, finally, to the compounds


, and


, respectively.

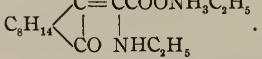
Clearly, such a double condensation, if it could occur at all, would, doubtless, depend essentially on the possibility of forming new cycloids of the maximum stability, *i. e.*, those containing five or six members. As will be seen from the second part of this paper, these ideas have been realized in the case of orthoaminophenol, whereas, in the case of the para compound, two molecules combined with one of the acid, the product being a salt of an addition product.

In connection with another line of work, it appeared to be desirable to investigate the behavior of camphoroxalic acid toward certain *tertiary bases*, especially those of an alkaloidal nature, the particular object being to obtain salts with well developed crystallizing power, which might ultimately prove of service in the examination of camphoroxalic acid for possible stereo- or structural isomers. Our results in this connection are discussed later in this present paper.

In previous communications on this subject[1] the interaction of camphoroxalic acid with methylamine, α-naphthylamine, β-naphthylamine, paratoluidine, metatoluidine, benzylamine, benzamidine, benzidine, 1,2,4–nitrotoluidine, orthophenylenediamine, aniline, semicarbazine, dimethylamine, diethylamine, hydroxylamine, ammonia, phenylhydrazine, urea, methylurea, symmetrical dimethylurea, unsymmetrical dimethylurea, hydrazine, and parabromphenylhydrazine has been studied. We have now supplemented this by the investigation of the following substances:

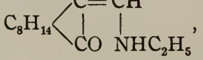
Primary Amines.

1. *Ethylamine.*—Ethylamine gives *ethylamine ethylcamphoformeneaminecarboxylate*,



$$C_8H_{14}\left\langle\begin{array}{ll} C = & CCOONH_3C_2H_5 \\ | & | \\ CO & NHC_2H_5 \end{array}\right. .$$

When this salt is heated considerably above its melting point, *ethylcamphoformeneamine*,



$$C_8H_{14}\left\langle\begin{array}{ll} C = & CH \\ | & | \\ CO & NHC_2H_5 \end{array}\right. ,$$

is formed.

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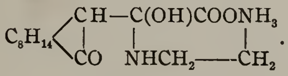
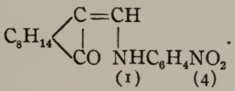
[1] *Loc. cit.*

2. *Ethylenediamine.*—Ethylenediamine gives a product resembling the direct addition products of primary amines with this acid which have been described by Bishop Tingle and his colleagues,[1] and is, accordingly, a *camphoformolamine derivative*, represented by the formula



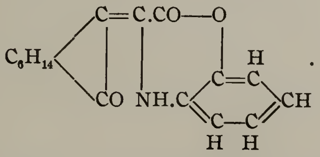
$$C_8H_{14}\!\left\langle\begin{array}{l}CH-C(OH)COONH_3 \\ |\qquad\;\; |\qquad\qquad\qquad\; | \\ CO\quad NHCH_2\text{——}CH_2\end{array}\right. .$$

3. *Paranitraniline.*—Paranitraniline gives *paranitrophenylcamphoformeneamine*,

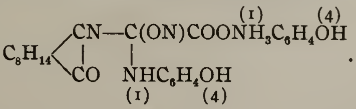


$$C_8H_{14}\!\left\langle\begin{array}{l}C=CH \\ |\qquad | \\ CO\;\; NHC_6H_4NO_2 \\ \qquad\;(1)\qquad\;\;(4)\end{array}\right. .$$

4. *Orthoaminophenol.*—Orthoaminophenol gives the lactone of *orthohydroxyphenylcamphoformeneaminecarboxylic acid*,



5. *Paraminophenol.*—Paraminophenol gives *paraminophenol parahydroxyphenylcamphoformolaminecarboxylate*,



$$C_8H_{14}\!\left\langle\begin{array}{l}\qquad\qquad\qquad\qquad\qquad\quad(1)\qquad\;\;(4) \\ CN-C(ON)COONH_3C_6H_4OH \\ |\qquad | \\ CO\;\; NHC_6H_4OH \\ \qquad(1)\qquad\;\;(4)\end{array}\right. .$$

Attempts were made to obtain compounds of camphoroxalic acid with *n-propylamine* (6), *metaphenylenediamine* (7), and *paraphenylenediamine* (8), but without success. Reaction appears to take place in each case, but the products cannot be purified by any of the ordinary methods. Even had it been worth while, time was lacking to devise a special mode of isolation for each compound.

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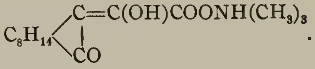
[1] *Loc. cit.*

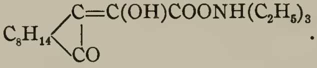
Tertiary Amines.

9. *Trimethylamine.*—Trimethylamine gives *trimethylamine camphoroxalate*,



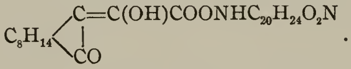
$$C_8H_{14}\left\langle\begin{array}{l} C{=}C(OH)COONH(CH_3)_3 \\ | \\ CO \end{array}\right. .$$

10. *Triethylamine.*—Triethylamine yields *triethylamine camphoroxalate*,



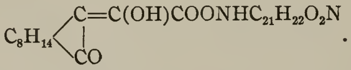
$$C_8H_{14}\left\langle\begin{array}{l} C{=}C(OH)COONH(C_2H_5)_3 \\ | \\ CO \end{array}\right. .$$

11. *Quinine.*—Quinine forms *quinine camphoroxalate*,



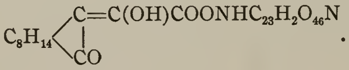
$$C_8H_{14}\left\langle\begin{array}{l} C{=}C(OH)COONHC_{20}H_{24}O_2N \\ | \\ CO \end{array}\right. .$$

12. *Strychnine.*—Strychnine gives *strychnine camphoroxalate*,



$$C_8H_{14}\left\langle\begin{array}{l} C{=}C(OH)COONHC_{21}H_{22}O_2N \\ | \\ CO \end{array}\right. .$$

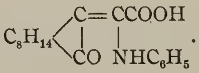
13. *Brucine.*—Brucine yields *brucine camphoroxalate*,



$$C_8H_{14}\left\langle\begin{array}{l} C{=}C(OH)COONHC_{23}H_2O_{46}N \\ | \\ CO \end{array}\right. .$$

Attempts to prepare two isomeric compounds were unsuccessful.

14. *Benzalaniline.*—Benzalaniline gives *phenylcamphoformeneaminecarboxylic acid*,



$$C_8H_{14}\left\langle\begin{array}{ll} C{=} & CCOOH \\ | & | \\ CO & NHC_6H_5 \end{array}\right. .$$

Its production is evidently due to a hydrolysis of the benzalaniline into benzaldehyde and aniline under the influence of the acid and of a trace of water in the reacting materials.

As the reaction proceeded the quantity of water would, of course, increase steadily, because it is necessarily formed as a result of the condensation. The presence of benzaldehyde among the products of the reaction was proved by its odor.

The formation of the above condensation product demonstrates once more, in the clearest manner, the superior reactivity of the enolic group C : COH, as compared with the carboxylic group, *i. e.*, even with relatively strong bases, if other conditions are favorable, condensation, rather than salt formation, takes place. Cf. p. 280.

15. *Piperine.*—Piperine gave only a small amount of piperic acid, owing, probably, to the presence of a little moisture in the reagents.

16. *Tribenzylamine.*—Attempts to obtain a crystalline salt of tribenzylamine and camphoroxalic acid were unsuccessful.

It is evident that, of the salts described above, those of brucine and strychnine appear to be admirably adapted for the investigation of possible isomeric forms of camphoroxalic acid. This matter will receive attention in the near future.

17. *Tetraethylammonium Hydroxide.*—Tetraethylammonium hydroxide gave a crystalline *salt*, but it was too unstable to permit of complete purification.

The following table (pp. 286–7) shows the various condensation compounds of camphoroxalic acid and primary amines which have been prepared by Bishop Tingle and his coworkers[1] and also those which are described for the first time in this paper. The former are indicated by an asterisk (*). Those marked + contain the elements of 1 molecule of water more than is shown by the type formula. When no definite compound could be isolated the space in the table is occupied by a dash.

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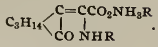
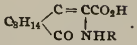
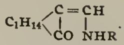
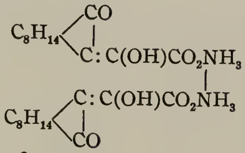
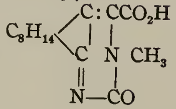
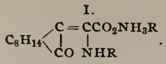
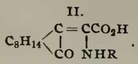
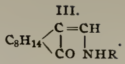
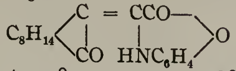
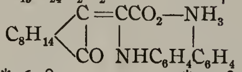
[1] *Loc. cit.*

	Primary amine.	I.  $C_3H_{14}\left<\begin{matrix}C=CCO_2NH_8R\\ \vert \quad\quad \vert \\ CO\ NHR\end{matrix}\right.$.	II.  $C_8H_{14}\left<\begin{matrix}C=CCO_2H\\ \quad\quad \vert \\ CO\ NHR\end{matrix}\right.$.	III.  $C_1H_{14}\left<\begin{matrix}C=CH\\ \vert \quad\ \vert \\ CO\ NHR\end{matrix}\right.$.
1	NH_3	.....	*178°	.....
2	NH_2OH	.....	+*146°.5	.....
3	CH_3NH_2	*172°	.....	*131°
4	$C_2H_5NH_2$	109°	.....	118°
5	n-$C_7H_7NH_2$	Gum was formed		
6	H_2NNH_2			*186°
7	$OC(NH_2)_2$	*192°–194°		
8	$CH_3NHCONH_2$			*154°
9	$(CH_3)_2NCONH_2$	.....	.....	.....
10	$H_2NCH_2CH_2NH_2$	.....	+220°	.....
11	$H_2NCONHNH_2$	.....	*198°	.....
12	$C_6H_5CH_2NH_2$	*147°.5	*140°	*96°.5
13	$C_6H_5NH_2$	*158°	*174°	*166°
14	$CH_3C_6H_4NH_2$(1 : 2)	.....	.....	.....

	Primary amine.	I.  $C_8H_{14}<\begin{array}{l}C=CCO_2NH_3R\\ \vert\qquad\vert\\ CO\ \ NHR\end{array}.$	II.  $C_8H_{14}<\begin{array}{l}C=CCO_2H\\ \vert\qquad\vert\\ CO\ \ NHR\end{array}.$	III.  $C_8H_{14}<\begin{array}{l}C=CH\\ \vert\qquad\vert\\ CO\ \ NHR\end{array}.$
15	$CH_3C_6H_4NH_2$(1:3)	*126°	*154°	.....
16	$CH_3C_6H_4NH_2$(1:4)	*152°	*168°	*178°
17	$HOC_6H_4NH_2$(1:2)	 $C_8H_{14}<\begin{array}{l}C = CCO-\\ \vert\qquad\ \ \vert\\ CO\ \ HNC_6H_4\end{array}>O$		*159°.5
18	$HOC_6H_4NH_2$(1:4)	+190°	178°	314°
19	$C_6H_4(NH_2)_2$(1:2)	$C_{18}H_{22}O_2N_2$	*246°	.....
20	$C_6H_4(NH_2)_2$(1:3)	.....	.....	.....
21	$C_6H_4(NH_2)_2$(1:4)	.....	.....	.....
22	$O_2NC_6H_4NH_2$(1:4)	.....	.....	156°
23	$CH_3COC_6H_4NH_2$(1:4)	.....	.....	.....
24	$CH_3C_6H_3(NO_2)NH_2$(1:2:4)	.....	.....	*192°
25	$C_6H_5NHNH_2$	.....	*120°	.....
26	$BrC_6H_4NHNH_2$(1:4)	.....	+*149°	.....
27	$C_6H_5C(:NH)NH_2$	$C_{19}H_{24}O_2N_2$	*184°	.....
28	$H_2NC_6H_4C_6H_4NH_2$(1:4)	 $C_8H_{14}<\begin{array}{l}C=CCO_2-NH_3\\ \vert\qquad\vert\qquad\quad\vert\\ CO\ \ NHC_6H_4C_6H_4\end{array}$		*190°
29	α-$C_{10}H_7NH_2$	*165°	*170°	.....
30	β-$C_{10}H_7NH_2$	*169°	*172°.5	*173°

Experimental.

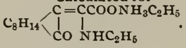
In the preparation of camphoroxalic acid the method used was that described by J. Bishop Tingle and W. E. Hoffman, Jr.,[1] with the changes which were suggested and employed by J. Bishop Tingle and C. J. Robinson.[2]

Primary Amines.

1. *Ethylamine.*—Ethylamine (5 grams = 2 mol.) and camphoroxalic acid (12.5 grams = 1 mol.) were placed in a pressure bomb with 30 cc. of absolute ethyl alcohol and heated to 100° for six hours. The bomb was opened after cooling and the excess of solvent evaporated. A semicrystalline mass was left which, on dissolving in gasoline and adding chloroform, separated from the solution in a fairly pure condition. The compound was purified by recrystallization from ethyl acetate, being deposited in white needles, which melt at 109°. When dissolved in alcohol and ferric chloride is added, no color is produced. Analysis showed the compound to be *ethylamine ethylcamphoformeneaminecarboxylate.*

Analysis:

0.2303 gram substance gave 19.2 cc. N at 24° and 760 mm.

	Calculated for  $C_8H_{14}<\begin{matrix}C=CCOONH_3C_2H_5\\ \vert \quad \vert\\ CO\ \ NHC_2H_5\end{matrix}$.	Found.
N	9.47	9.13

When treated with sodium hydroxide the above salt dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and ethylamine.

When heated at 150° *ethylamine ethylcamphoformeneaminecarboxylate* gives off carbon dioxide and ethylamine and forms a compound which, when recrystallized from acetone, is deposited in semitransparent plates, melting at 118°. With alcoholic ferric chloride no color reaction is produced. Analysis proved this compound to be *ethylcamphoformeneamine.*

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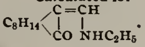
[1] This Journal, **34**, 235 (1905).

[2] *Ibid.*, **35**, 248 (1906).

Analysis:

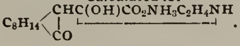
0.1135 gram substance gave 7.0 cc. N at 24° and 755 mm.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C=CH\\CO\quad NHC_2H_5\end{array}\right.$.	Found.
N	6.77	6.70

2. *Ethylenediamine.*—The free base was prepared as follows: Ethylenediamine hydrochloride (5 grams = 1 mol.) was dissolved in absolute methyl alcohol. To this was added an alcoholic solution of potassium hydroxide containing 42 grams = 2 mol. The alcoholic solution of the base was filtered from the potassium chloride and to the solution camphoroxalic acid (8.4 grams = 1 mol.) was added and the liquid heated for a short time. Crystals began to form and the solution was concentrated further in a vacuum desiccator. The compound was purified by crystallization from a mixture of 60 parts of methyl alcohol and 40 parts of water, being deposited in greyish-white, microscopic crystals, melting at 220°. It is sparingly soluble in ethyl acetate, acetone, benzene, toluene, ether, and in ethyl and methyl alcohols. Analysis showed the substance to be an additive compound similar to the body obtained by Bishop Tingle[1] from hydroxylamine and camphoroxalic acid, and it belongs to the *camphoformolamine series.*

Analysis:

0.1816 gram compound gave 15.3 cc. N at 770 mm. and 20°.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}CHC(OH)CO_2NH_3C_2H_4NH\\CO\end{array}\right.$.	Found.
N	9.87	9.58

When the above compound is heated at 215° water and carbon dioxide are given off and a dark gummy mass is left in the tube. A semicrystalline mass was separated from this but no crystals free from gum could be obtained, so that no attempt was made to analyze the compound. The gummy mass gave no color reaction with alcoholic ferric chloride.

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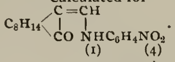
[1] *Loc. cit.*

3. *Paranitraniline.*—Paranitraniline (4.15 grams = 1 mol.), camphoroxalic acid (6.75 grams = 1 mol.), and benzene (30 cc.) were heated, under pressure, at 135°-140°, for six hours. When the bomb was opened, after cooling, there was considerable internal pressure. The benzene was evaporated and a tarry mass was formed. As no crystals could be separated from this tar by dissolving it in various solvents, it was treated with a dilute aqueous solution of sodium carbonate. The part insoluble in the carbonate solution was dissolved in benzene and ligroin was added. Crystals separated and were further purified by recrystallization from alcohol, being deposited as glistening, brownish-yellow needles, melting at 156°. Analysis of this compound showed it to be *paranitrophenylcamphoformeneamine.*

Analysis:

I. 0.1737 gram substance gave 14.8 cc. N at 761 mm. and 19.5°.

II. 0.1108 gram substance gave 0.2772 gram CO_2 and 0.0665 gram H_2O.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll} C & = CH \\ \vert & \quad\vert \\ CO & NHC_6H_4NO_2 \\ & (1) \qquad (4) \end{array}\right.$	Found.	
		I.	II.
C	68.00	....	68.23
H	6.66	....	6.66
N	9.33	9.61	....

With alcoholic ferric chloride no color reaction is obtained.

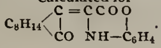
On acidification of the sodium carbonate solution mentioned above with dilute hydrochloric acid, camphoroxalic acid is deposited.

4. *Orthoaminophenol.*—Orthoaminophenol hydrochloride (5.8 grams = 2 mol.) and camphoroxalic acid (4.5 grams = 1 mol.) were heated in alcoholic solution until crystals began to form. These were purified by recrystallization from ethyl acetate, being deposited in well-defined yellow crystals belonging to the monoclinic system and melting at 159°.5. Analysis of this compound showed it to be the *lactone* of *orthohydroxyphenylcamphoformeneaminecarboxylic acid.*

Analysis:

I. 0.1277 gram substance gave 0.0772 gram H_2O and 0.3413 gram CO_2.

II. 0.1871 gram substance gave 8.2 cc. N at 750 mm. and 20°.

	Calculated for	Found.	
		I.	II.
C	72.67	72.89	....
H	6.45	6.71	....
N	4.72	....	4.85

The compound is practically insoluble in water, readily soluble in barium hydroxide solution, and slightly soluble in sodium carbonate solution.

When heated to 290° the substance sublimes, forming long, silky, yellow needles which have the same melting point as the original crystals, *i.e.*, 159°.5. On heating the compound with one molecular proportion of barium oxide at 290° for forty-five minutes, a tarry mass was formed from which no crystals could be obtained. Some of the compound described above was dissolved in aqueous barium hydroxide solution and boiled for five minutes, then a little alcohol was added and the solution allowed to stand overnight. It was then acidified with dilute hydrochloric acid and crystals separated. After washing them with water and drying, they melted at 155°-157°, and on recrystallizing the compound once from ethyl acetate the product melted at 159°.5, showing that this treatment with alkali has caused no change. The substance is, therefore, evidently a lactone.

With alcoholic ferric chloride no color reaction was produced.

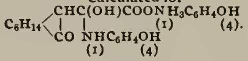
5. *Paraminophenol.*—Paraminophenol (5 grams = 2 mol.), camphoroxalic acid (5 grams = 2 mol.), and absolute alcohol (40 cc.) were heated under pressure for two hours, at 105°-110°. A few crystals had separated on cooling, and a further portion was obtained on concentrating the solution. Recrystallization from alcohol caused the compound to be deposited in light, yellow, feathery crystals, melting at 190° and decomposing when heated above the melting point. Analysis of

this substance showed it to be *paraminophenol parahydroxy phenylcamphoformolaminecarboxylate.*

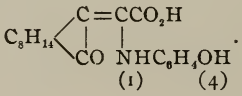
Analysis:

I. 0.1083 gram substance gave 0.2587 gram CO_2 and 0.0708 gram H_2O.

II. 0.1647 gram substance gave 9.1 cc. N at 761 mm. and 23°.

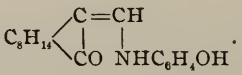
	Calculated for  $C_6H_{14}\left\langle\begin{array}{l} CHC(OH)COONH_3C_6H_4OH \\ \qquad\qquad\qquad\quad (1) \qquad\quad (4). \\ \mid \quad \mid \\ CO\ NHC_6H_4OH \\ \quad\ (1) \quad\ (4) \end{array}\right.$	Found. I.	Found. II.
C	65.11	65.14	....
H	6.83	7.26	....
N	6.34	....	6.09

When the compound described above is heated for a short time with dilute hydrochloric acid, the crystals become yellow but do not go into solution. Purified by crystallizing from benzene, the compound melts and decomposes at 178°. No analysis was made of this substance, but from the mode of formation and its properties there can hardly be any doubt that it is *parahydroxyphenylcamphoformeneaminecarboxylic acid,*



$$C_8H_{14}\left\langle\begin{array}{l} C=CCO_2H \\ \mid \qquad \mid \\ CO\ NHC_6H_4OH \\ \quad\ (1) \qquad (4) \end{array}\right. .$$

When this acid is heated above its melting point, carbon dioxide is eliminated and a gum is left which, after solution in benzene, separates in greyish, microscopic crystals, softening at 305° and melting at 314°. From its mode of formation this compound is evidently *parahydroxyphenylcamphoformeneamine,*



$$C_8H_{14}\left\langle\begin{array}{l} C=CH \\ \mid \qquad \mid \\ CO\ NHC_6H_4OH \end{array}\right. .$$

6. *Propylamine.*—Propylamine and camphoroxalic acid were mixed in the proportion of 2 molecules of the amine to 1 of the acid and heated in alcoholic solution, so as to prepare a condensation compound. A gummy mass was formed from which no definite compound could be isolated. Sodium cam-

phoroxalate was also tried with propylamine in alcoholic solution but with no better results. These experiments were made before our work[1] on secondary amines was completed. In view of some of the results with aliphatic amines which are described in that paper, there can be little doubt that propylamine and camphoroxalic acid condense to form a liquid compound which could probably be purified by distillation under diminished pressure. Unfortunately there was no time to test this idea.

7. *Metaphenylenediamine.*—Attempts to prepare condensation compounds with this amine and camphoroxalic acid were carried out as follows: The amine hydrochloride (1 mol.), camphoroxalic acid, (1 mol.), and potassium hydroxide (2 mol.) were heated under pressure with absolute alcohol at 130° for 5 hours. After freeing the solution from the potassium chloride formed, it was attempted to purify the crystals separating from the alcohol by using various solvents, but they were contaminated with inorganic matter from which they could not be freed. Consequently they gave no definite melting point and no concordant analytical results.

8. *Paraphenylenediamine.*—The experiments with this compound were made in a similar manner to those with the meta derivative, the results being essentially the same. There is no doubt that, in both cases, a reaction takes place. The compounds which are likely to have been formed are not, however, at present of sufficient importance to us to justify the large expenditure of time and material which would be needed for their isolation, consequently the matter was not pursued further.

Tertiary Amines.

9. *Trimethylamine.*—Trimethylamine hydrochloride (4 grams = 1 mol.) was dissolved in absolute methyl alcohol. To this was added potassium hydroxide (2.35 grams = 1 mol.), also in absolute methyl alcohol solution, to liberate the base. The potassium chloride was separated and to the solution camphoroxalic acid (9.5 grams = 1 mol.) was added.

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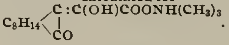
[1] THIS JOURNAL. 39, 105 (1908).

Without further heating the alcohol was evaporated over sulphuric acid in a vacuum desiccator. The resulting compound was purified by crystallization from benzene, being deposited in white, microscopic crystals melting and evolving gas at 139°–140°. With alcoholic ferric chloride a violet color is produced. The compound dissolves in aqueous sodium bicarbonate solution with evolution of gas. Analysis showed the substance to be *trimethylamine camphoroxalate.*

Analysis:

0.1833 gram substance gave 7.9 cc. N at 24°.5 and 771 mm.

	Calculated for  $C_8H_{14}\left<\begin{array}{l}C:C(OH)COONH(CH_3)_3\\ \;|\\ CO\end{array}\right.$.	Found.
N	4.95	4.77

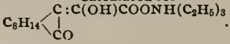
When the preceding compound is heated above its melting point a gum is formed from which it was impossible to isolate a crystalline derivative.

Triethylamine.

10. Triethylamine.—Triethylamine hydrochloride (2 grams = 1 mol.), camphoroxalic acid (3.3 grams = 1. mol.), and potassium hydroxide (0.8 gram = 1 mol.) were mixed and heated in absolute ethyl alcohol. A precipitate of potassium chloride was formed and was separated from the solution, which was then concentrated. The resulting solid was dissolved in benzene and ligroin added. On standing, crystals separated. These were recrystallized several times from benzene, being deposited in small, white needles melting at 102°–103°. With alcoholic ferric chloride, a violet color is produced. The compound dissolves in aqueous sodium carbonate solution with the evolution of gas. As the yield was small, the reaction was repeated under conditions similar to those with trimethylamine, whereupon the yield was very good. Analysis of this compound showed it to be *triethylamine camphoroxalate.*

Analysis:

0.1702 gram substance gave 6.6 cc. N at 23°.5 and 767 mm.

	Calculated for  $C_8H_{14}\left<\begin{array}{l}C:C(OH)COONH(C_2H_5)_3\\ \;|\\ CO\end{array}\right.$.	Found.
N	4.31	4.27

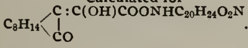
When this compound is heated above its melting point a gummy mass is formed which, when dissolved in ethyl acetate, deposits crystals, but these could not be obtained with a definite melting point, nor could concordant analyses of them be made.

11. Quinine.—Quinine (5 grams = 1 mol.) and camphoroxalic acid (4 grams = 1 mol.) were dissolved in benzene. The solution was then allowed to remain at the ordinary temperature for 24 hours. At the end of this time the crystals had separated. These were purified by crystallization from ether, being deposited as white, microscopic crystals melting and evolving gas at 160°–161°. With alcoholic ferric chloride solution a violet color is produced. Analysis showed the compound to be *quinine camphoroxalate.*

Analysis:

I. 0.1403 gram substance gave 0.3605 gram CO_2 and 0.0951 gram H_2O.

II. 0.2028 gram substance gave 9.2 cc. N at 25°.5 and 755 mm.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C:C(OH)COONHC_{20}H_{24}O_2N\\ \vert\\ CO\end{array}\right.$.	Found. I.	 II.
C	70.02	70.07	....
H	7.35	7.53	....
N	5.12	....	4.88

When this salt is heated above its melting point a gum is formed, from which no crystals could be obtained. This gum was treated with an aqueous sodium carbonate solution and extracted with ether. Free quinine was isolated from the ethereal solution and, on acidifying the sodium carbonate solution with dilute hydrochloric acid, camphoroxalic acid separated.

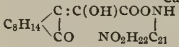
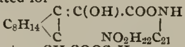
12. Strychnine.—Strychnine (5 grams = 1 mol.) and camphoroxalic acid (3.4 grams = 1 mol.) were dissolved in benzene and allowed to stand at room temperature for 18 hours. Crystals were formed and these were purified by recrystallization from ethyl acetate, being deposited as small, white needles melting and evolving gas at 214°–215°. With alcoholic ferric chloride solution a violet color is produced. Analysis showed this compound to be *strychnine camphoroxalate* and that it crystallizes with 0.5 molecule of ethyl acetate.

Analysis:

I. 0.2420 gram substance gave 0.6147 gram CO_2 and 0.1556 gram H_2O.

II. 0.1884 gram substance gave 7.8 cc. N at 23°.5 and 763 mm.

III. 0.7691 gram substance lost 0.0513 gram on heating at 104°.

	Calculated for		Found.	
	 $C_8H_{14}\left\langle\begin{matrix}C:C(OH)COONH \\ CO \quad NO_2H_{22}C_{21}\end{matrix}\right.$	 $C_8H_{14}\left\langle\begin{matrix}C:C(OH).COONH \\ C \quad NO_2H_{22}C_{21}\end{matrix}\right.$ $+0.5\ CH_3COOC_2H_5$.	I.	II.
C	70.91	69.10	69.27	....
H	6.85	7.18	7.14	....
N	5.02	4.75	....	4.62

Calculated for 0.5 $CH_3COOC_2H_5$.	Found. III.
6.79	6.67

When the preceding compound is heated above its melting point the odor of camphor is quite noticeable on opening the tube. After removal of the camphor a gum is left from which no crystalline derivative could be isolated.

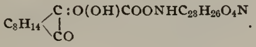
13. Brucine.—With brucine and camphoroxalic acid it was attempted to obtain two isomeric compounds, and with this end in view the reaction was carried out as follows:

Brucine (2.5 grams = 0.5 mol.) was dissolved in hot benzene. To this camphoroxalic acid (2.8 grams = 1 mol.) was added. The solution was allowed to cool and crystals were soon deposited. These were filtered off and to the solution a second quantity of brucine (2.5 grams = 0.5 mol.) was added, the liquid being heated to dissolve the brucine. On cooling, crystals were formed. These were separated and were found to be identical with the first portion. The compound was purified by recrystallization from alcohol, being deposited in small, glistening, white plates melting and evolving gas at

235°–236°. The substance gives a violet color with alcoholic ferric chloride solution. Analysis of the compound proved it to be *brucine camphoroxalate.*

Analysis:

0.1822 gram substance gave 7.7 cc. N at 24°.5 and 764 mm.

	Calculated for  $C_8H_{14}\begin{matrix}/C:O(OH)COONHC_{28}H_{26}O_4N\\ \vert\\ \backslash CO\end{matrix}$.	Found.
N	4.54	4.63

This shows that brucine, as well as quinine and strychnine, readily forms salts with camphoroxalic acid and that, under the conditions employed, no isomeric derivatives are produced. This matter will receive further attention subsequently.

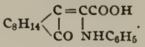
When the brucine salt is heated above its melting point, water and carbon dioxide are given off and the odor of camphor is very pronounced. A gummy mass is left in the tube, from which no crystals could be isolated by the use of ordinary solvents. The gum was treated, finally, with dilute sodium carbonate solution and extracted with ether. A very small amount of material was dissolved in the ether. Some of it, which did not dissolve in the carbonate solution, was recrystallized and found to be impure brucine. On acidifying the carbonate solution with dilute hydrochloric acid a small amount of camphoroxalic acid separated. Evidently the salt had decomposed under the conditions of the heating and subsequent treatment.

14. Benzalaniline.—Benzalaniline (4 grams = 1 mol.), camphoroxalic acid (5 grams = 1 mol.), and absolute alcohol (30 cc.) were heated under pressure at 120°, for two hours. On evaporating the alcohol a gummy mass was left, but when this was dissolved in benzene and ligroin was added, crystals separated. These were purified by recrystallization from benzene, separating as yellow, microscopic crystals melting at 174°. Analysis showed this compound to be *phenylcamphoformeneaminecarboxylic acid.*

Analysis:

I. 0.1035 gram substance gave 0.2740 gram CO_2 and 0.0734 gram H_2O.

II. 0.1807 gram substance gave 7.8 cc. N at 22° and 762 mm.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C=CCOOH\\ \vert\qquad \vert\\ CO\;\; NHC_6H_5\end{array}\right.$.	Found.	
		I.	II.
C	72.24	72.20	....
H	7.02	7.87	....
N	4.68	....	4.79

This compound was found to be identical with that prepared by Bishop Tingle[1] from aniline and camphoroxalic acid. Comparative melting points were made on the compound from benzalaniline and aniline by using three capillary tubes, containing, respectively, the compounds from benzalaniline, and from aniline, and a mixture of the two. The three tubes were heated at once and the substance in each melted at the same point, namely, 174°. As has been pointed out before, such comparisons are necessary to establish the identity of many compounds of this series, because the melting point depends greatly on the rapidity with which the substances are heated. It is evident that, under the conditions employed, benzalaniline is hydrolyzed to its constituents, the aniline combining with the camphoroxalic acid and the benzaldehyde remaining in the free state. The bearing of this fact on the general course of the condensation of camphoroxalic acid with bases is pointed out in the theoretical portion of this paper.

Another attempt to prepare a condensation product from camphoroxalic acid and benzalaniline was made as follows:

Benzalaniline (5.5 grams = 1.5 mol.), sodium camphoroxalate (5 grams = 1 mol.), and 40 cc. of anhydrous benzene, which had been dried over sodium, were heated under pressure for four hours, at 105°–108°. When the benzene was evaporated in a vacuum desiccator over sulphuric acid, a gummy mass was left. As no crystals could be separated by dissolving the product in ordinary solvents, it was dissolved in alcohol and acidified with dilute acetic acid. After being freed from the sodium acetate, the solution was concentrated and a gum was formed. This was dissolved in benzene and sodium carbonate added. On acidifying the sodium carbonate solution with dilute hydrochloric acid, a yellow precipitate was deposited. This was purified by recrystallizing from benzene and was found to be identical with the compound obtained in the former experiment.

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[1] This Journal, **21**, 238 (1899).

15. Piperine.—Piperine (7.1 grams = 1 mol.), camphoroxalic acid (6.7 grams = 1 mol.), and benzene (60 cc.) were heated under pressure at 165° for five hours. Some crystals had separated when the bomb was opened.

These were recrystallized from alcohol and were deposited in light yellow needles, softening at 210° and melting at 217°. The color, form, and melting point of these crystals correspond exactly with those of piperic acid.

On concentrating the solution from the bomb, crystals were deposited. These were recrystallized from alcohol and were found to be unchanged piperine.

An analysis for nitrogen was made with the compound before its nature was known but, of course, none was found.

The piperic acid was formed in very small quantity. Its production is doubtless due to traces of moisture in the materials and vessel used in the experiment.

16. Tribenzylamine.—Tribenzylamine and camphoroxalic acid were heated, in alcoholic solution, on the water bath, and a gum was formed from which we were unable to isolate a crystalline compound with a definite melting point. A semicrystalline mass was separated from the gum, but it could not be obtained in a pure condition. On treating this with sodium carbonate and extracting with ether, free tribenzylamine was obtained from the ethereal solution. The sodium bicarbonate solution was acidified with dilute hydrochloric acid and camphoroxalic acid separated, showing that the treatment with carbonate had decomposed the semicrystalline mass. The latter must, therefore, have consisted of *tribenzylamine camphoroxalate.*

17. *Tetraethylammonium Hydroxide.* — Tetraethylammonium hydroxide, 10 per cent aqueous solution, and camphoroxalic acid were mixed in 95 per cent alcohol and heated for a short time. The alcohol was allowed to evaporate spontaneously and the residue was crystallized from benzene, being deposited in glistening white needles. These give a violet color with ferric chloride solution. Attempts were made to analyze this compound, but it decomposes so easily that no concordant results could be obtained. It is, doubtless, *tetraethylammonium camphoroxalate.*

We desire to express our grateful thanks to the Trustees of the Warren Research Fund of the American Academy of Arts and Sciences for a grant to defray a part of the cost of some of the chemicals used in the investigation recorded in the preceding pages.

The work described in this paper has been carried out at the Johns Hopkins University. It will be continued by the senior author at this university.

McMaster University,
Toronto, Canada,
July, 1907.

ON THE REACTIONS OF CARBONYL COMPOUNDS WITH HYDROXYLAMINE AND HYDROXYLAMINE HYDROCHLORIDE.

[SEVENTH COMMUNICATION ON CATALYSIS.[1]]

By S. F. Acree.

(The writer is indebted to the Carnegie Institution of Washington for aid in this work.)

The recent articles by Abel,[2] Lapworth,[3] Landrien,[4] and Euler[5] bear so directly on our investigations on catalysis which are being conducted in this laboratory that the writer wishes to record the following comments:

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[1] Acree and Hinkins: This Journal, **28**, 370; Dental Cosmos, June, 1901. Acree and Johnson, This Journal, **37**, 410; **38**, 258. Acree and Nirdlinger: *Ibid.*, **38**, 489. Acree, Johnson, and Nirdlinger: *Ibid.*, **38**, 746.

[2] Z. Elek. Chem., **13**, 555.

[3] J. Chem. Soc., **91**, 1133.

[4] Compt. rend., **140**, 1392.

[5] Z. physiol Chem., **52** 146.

Abel showed that the apparently noncatalyzed reaction between hydrogen peroxide and thiosulphates proceeds with *measurable* rapidity. The reaction velocity is increased by the presence of iodide ions because the hydrogen peroxide, reacting with them with a measurable velocity, forms a small amount of the iodoso ion, which reacts with immeasurable rapidity with the thiosulphate and hydrogen ions.

The work of Abel is certainly of the very greatest importance as it gives us another example in which the purely catalytic reactions, as defined by Ostwald,[1] such as inversion of cane sugar, hydrolysis of esters by acids, etc., are connected with the clear-cut cases of catalytic changes through reactions of measurable amounts of intermediate products formed by the reaction or union of the catalyzer with some other substance present. The discovery of other similar cases is very much to be desired. To Abel's list of such catalytic reactions through measurable amounts of intermediate products should be added the work of Stieglitz[2] on the hydrolysis of imidoester cations, that of Acree and Johnson[3] and of Acree and Shadinger[4] on the negative catalysis which is produced by the influence of hydrogen and other cations on the reactions between alkyl halides and urazole anions, and the investigation of Acree and Johnson on the reactions of carbonyl compounds with hydroxylamine and hydroxylamine salts.

The writer wishes to lay special stress on several characteristic features of the reactions between carbonyl compounds and hydroxylamine which have been met with for the first time in the study of catalytic reactions. It should be pointed out briefly that the data of Acree and Johnson seem to show that acetone and hydroxylamine in aqueous solutions unite very readily and nearly completely, as illustrated in the following expressions,

$$(CH_3)_2CO + NH_2OH \rightleftarrows (CH_3)_2C{=}NOH + H_2O, \text{ or}$$

$$\frac{dx}{dt} = K(A - x)\ (B - x) - K'(C_{H_2O} + x)x \qquad (1),$$

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[1] Lehrbuch der allgemeinen Chemie, II (2), 262. Z. Elek. Chem., **7**, 995.

[2] Congress of Arts and Science, St. Louis, 1904, **4**, 276.

[3] This Journal, **38**, 259.

[4] See the article in this number of This Journal.

and that the velocity of the reaction is accelerated by acids because the hydroxylamine or the acetone forms cations which are much more reactive than the free bases:

$$(CH_3)_2CO + \overset{+}{N}H_3OH \rightleftarrows (CH_3)_2C = \overset{+}{N}HOH + H_2O \quad (1'),$$

or

$$(CH_3)_2\overset{|}{C}—\overset{+}{O}H + NH_2OH \leftrightarrows (CH_3)C = \overset{+}{N}HOH + H_2O \quad (1'').$$

As it is not known with certainty at present whether reaction (1′) or (1″) is the correct one, we shall use (1′).

The quantitative data seem to show beyond question that the *free bases*, hydroxylamine and acetoxime, as well as their *cations*, enter into the reactions. In the case of the inversion of cane sugar, hydrolysis of esters, and hydrolysis of amides by acids, however, the substance chiefly undergoing transformation is the salt or cation formed by the union of small amounts of sugar, ester, or amide with corresponding amounts of acid or hydrogen ions, as has been brought out also by Lapworth,[1] Euler,[2] Bredig,[3] Kastle,[4] Stieglitz,[5] Acree and Johnson,[6] and Goldschmidt.[7] But in the change of acylhalogenaminobenzene derivatives into halogenacetanilides in the presence of acids, the substance transformed directly is the *undissociated salt* formed by the union of the acid and acylhalogenaminobenzene. *Whether the free base, dissociated salt, or undissociated salt undergoes transformation depends simply upon the relative activity of each in the particular reaction.*

1. The noncatalyzed reaction between acetone and hydroxylamine takes place with an easily measured rapidity, and the reaction is slightly reversible. This case and Abel's are, as far as the writer knows, the first[8] in which the noncatalyzed reactions could be measured accurately. Acree and Johnson, and Acree and Nirdlinger pointed out repeatedly

[1] Mellor's "Statics and Dynamics," 1904, p. 289.

[2] Z. physiol Chem., **52**, 146. Z. physik Chem., **36**, 405, 663; **40**, 501; **47**, 356.

[3] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528.

[4] THIS JOURNAL, **19**, 894; P. Am. Assn. Adv. Sci., **47**, 238; and original paper.

[5] Congress of Arts and Science, St. Louis, 1904, **4**, 276.

[6] *Loc. cit.*

Goldschmidt and Sunde: Ber. d. Chem. Ges., **39**, 711. Goldschmidt and Udby: Z. physik. Chem., **60**, 728.

[8] Miller and Clark: J. Physic. Chem., **11**, 353.

that a characteristic feature of the catalytic changes involved in the inversion of cane sugar, hydrolysis of esters, and hydrolysis of amides, is that the *free base* and the *undissociated salt* do not enter appreciably into the reaction, and that the catalyzed reaction, involving the reactions of the cations, is, for all practical purposes, the one actually being measured.[1]

The importance of such cases as that discovered by himself, as well as by Acree and Johnson, has not been overemphasized by Abel. It is only by having all possible conceivable cases, such as a measurable noncatalyzed reaction, a measurable rapidity of formation of the intermediate products, a measurable rapidity of the reactions of the intermediate products, and similar conditions with reversible reactions, that we can be sure ultimately of the fundamental concepts concerning catalytic reactions.

2. When the amount of catalyzer (hydrogen ions) which is added is insufficient to use up all of the base, hydroxylamine and acetoxime, the noncatalyzed and the catalyzed reactions take place side by side, each with measurable rapidity. If the NH_2OH reacts with the acetone, as in (1) and (1′), the total reaction velocity would then be, in dilute solutions in which C_{H_2O} does not change appreciably,

$$\frac{d(x+x')}{dt} = K(C_{acetone} - x - x')(C_{NH_2OH} - x) - K'x + K''(C_{acetone} - x - x')(C^{+}_{NH_3OH} - x') - K'''x' \quad (2).$$

It is seen at once that the second law of catalysis[2] can not hold in such a case, nor in the rearrangement of acylhalogenaminobenzene or the reactions worked out by Abel and by Miller and Clark; *the reaction velocity cannot be proportional to the concentration of the catalyzer.*[3] Abel, however, did not seem to see the importance of this point, which was brought out for the first time by Acree and Johnson. The only difference, aside from the reversibility of the reaction, between this case and Abel's is that the intermediate compound, $\overset{+}{N}H_3OH$ or $(CH_3)_2{=}\overset{+}{N}HOH$, is formed with immeasurable rapidity and is transformed with a measurable rapidity, whereas Abel's intermediate iodoso ion is formed with measurable rapidity and is decomposed with immeasurably high velocity.

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[1] Miller: J. Physic. Chem., **11**, 9.

[2] Acree and Johnson: THIS JOURNAL, **38**, 348 *et seq.*

[3] The reaction velocity and concentration of the catalyzer can be apparently proportional in two cases: (*a*) When the velocity of the noncatalyzed reaction is negligible and the catalyzer reacts completely with some constituents of the noncatalyzed reaction, as in the oxime work, where the reaction velocity is apparently proportional to the concentration of the catalyzer if there is present not more than one molecule, or ion, of the catalyzer to each one of the constituent with which it first reacts (Acree and Johnson: *Loc. cit.*, p. 350). (*b*) When the velocity of the noncatalyzed reaction and the con-

It is at once apparent that any reaction that seems to be of a given order and furnishes definite end products may really consist of (1) many reactions having the same order and velocity and giving the same measured end products; or of (2) one chief reaction of the order and approximate velocity measured, complicated by other reactions which have very small velocity constants and which yield the same end products.

(3) Mr. L. J. Desha has found that when an alkali is added to a solution of hydroxylamine and acetone the reaction is greatly accelerated and goes practically, if not entirely, to completion. The equilibrium point produced by alkali catalyzers,

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centration of the *active molecules of catalyzer-substance* (Acree, Johnson, and Nirdlinger: This Journal, **38**, 747) are negligible, and only one molecule or ion, of the catalyzer unites with one molecule of the other substance, and one molecule, or ion, of this *catalyzer-substance* reacts with other substances present, the reaction velocity and the concentration of the catalyzer will be proportional under the mathematical conditions discussed by Acree and Johnson. When n molecules, or ions, of the catalyzer or *catalyzer-substance* enter into the chemical changes the reaction velocity is proportional to Cat^n under the conditions discussed before. Even an apparently simple reaction might become quantitatively very complicated. If one molecule each of A, B, and Cat give one molecule each of the end products C, D, and Cat, under the above conditions, then

$$\frac{dx}{dt} = K(A-x)^p(B-x)^q Cat^r, \text{ when}$$

$$pA.rCat \underset{\textit{very rapid}}{\rightleftarrows} pA + rCat \text{ always holds, and}$$

$$qB + pA.rCat \underset{\textit{very slow}}{\longrightarrow} C + D + (p-1)A + (q-1)B + rCat.$$

In other words, the reaction velocity is proportional to the powers p, q, and r of the concentrations of A, B, and Cat, respectively, and not to the simple concentrations. Other similar cases will be given later. This can at once be extended to reversible reactions in which the equilibrium point will change with variations in the concentrations of the reacting substances and the catalyzer, as has already been shown by Acree and Johnson, by Abel, and by Euler. As stated before, these cases in the study of catalysis will be reported later in detail.

then, is different from that produced by acid catalyzers having the same concentration. The alkali probably forms small amounts of oxyammonium anions, $NH_2\overset{-}{O}$, which react much more rapidly with acetone than does the hydroxylamine. A stronger acid, acetoxime, is formed:

$$(CH_3)_2CO + NH_2OH + \overset{+}{K} + \overset{-}{OH} \rightleftarrows (CH_3)_2CO + NH_2\overset{-}{O} + \overset{+}{K} + H_2O \rightleftarrows (CH_3)_2C = N\overset{-}{O} + \overset{+}{K} + 2H_2O \quad (3).$$

It must be pointed out, however, that the acetone *may* form a salt whose anions react with the hydroxylamine.

$$(CH_3)_2CO + \overset{+}{K} + OH + NH_2\overset{-}{O}H \rightleftarrows (CH_3)_2C(OH)\,\overset{-}{O} + NH_2OH + \overset{+}{K} \rightarrow (CH_3)_2C = N\overset{-}{O} + \overset{+}{K} + 2\,H_2O.$$

With three solutions, made by adding 5 cc. N potassium hydroxide, 10 cc. 0.1 N potassium hydroxide, and 3 cc. 0.1 N potassium hydroxide, respectively, to 50 cc. each of 0.1 N hydroxylamine and 0.1 N acetone, and diluting to 110 cc., the constants for the reaction at 8° were approximately 1.50, 0.30, and 0.08. The velocity constant for the noncatalyzed reaction at 8° is negligible here and in equation (2). The constant is therefore practically directly proportional to the concentration of the catalyzer.

Since the hydroxylamine, or acetone, is a very weak acid[1] and is not converted completely into anions, the above catalyzed and the noncatalyzed reactions of hydroxylamine with acetone take place side by side as discussed in section (2). Indeed, the apparently noncatalyzed reaction (1) may take place because hydroxylamine itself, as an amphoteric compound, forms anions and cations of itself or acetone, which then react with acetone or hydroxylamine:

$$NH_2OH + NH_2OH \rightleftarrows \overset{+}{N}H_3OH + N\overset{-}{H}_2O \quad (4).$$

This possibility will be studied experimentally. /

The noncatalyzed reaction between acetone and hydroxylamine takes place with measurable rapidity. Both bases and acids increase the reaction velocity very greatly[1] through the formation of intermediate anions and cations of hydroxylamine or acetone and the reaction of these ions with the acetone or hydroxylamine. This is the first catalytic reaction in a homogeneous system in which both bases and acids are known to accelerate a reversible reaction, and in which the equilibrium point varies not only with the nature of the catalyzer but also with the amount of it. Much acid produces an equilibrium in which much salt of the stronger base, hydroxylamine, is formed. When the hydrogen ions are decreased to an amount equal to those present in water, less than 10 per cent of the hydroxylamine remains. When the alkali is added, still more of the salt of the stronger acid, acetoxime, is formed, and the hydroxylamine practically disappears. Nevertheless, each one of the three reactions seems to be reversible, the equilibrium point depending upon the nature and amount of the catalyzer. The ideas discussed in sections (2) and (4) hold perfectly well for the catalysis of this reaction by bases.

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[1] Lobry de Bruyn: Rec. Trav. Chim., **11**, 32. Hofmann and Kohlschütter: Z. anorg. Chem., **16**, 463. Bacon and Freer: THIS JOURNAL, **38**, 367.

These ideas make clear the fact,[2] discovered by Acree and Hinkins and by Bodenstein and Dietz, that the equilibrium point produced in the hydrolysis of esters by enzymes is different from that produced by acids. Enzymes probably accelerate such esterification and saponification reactions through the influence of the acid and basic groups in them.

It may be possible that the hydroxylamine anions and cations, $\overset{-}{NH_2O}$ and $\overset{+}{N}H_3OH$, really accelerate the reaction between the acetone and free hydroxylamine, just as in certain other cases salts[3] bring about catalytic reactions. In any event these phenomena are exactly analogous to the increased velocity of formation of anilides from aniline and organic acids in the presence of the halogen acid salts of aniline, and to the action of alkalis in increasing the rapidity of formation of thioureas from amines and carbon disulphide. We shall discuss these in detail in a subsequent article.

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[1] Professor Lapworth has just informed me privately that he has observed the same facts.

[2] Acree and Hinkins: This Journal, **28**, 370. Z. Elek. Chem., **12**, 605. Dietz: Dissertation, Leipzig, 1907.

[3] Acree and Johnson: This Journal, **38**, 259 *et seq.* Acree and Nirdlinger: *Ibid.*, **38** 489. Acree and Shadinger: *Ibid.*, **39**, 226. Arrhenius: Z. physik. Chem., **1**, 110; **4**, 226; **31**, 197. Euler: *Ibid.*, **32**, 348; Ber. d. Chem. Ges., **39**, 2726. Koelichen: Z. physik. Chem., **33**, 129.

We can predict that other cases will be found in which the presence of ammonium salts causes an increase or decrease in the velocity of the action of amino derivatives on carbonyl compounds.

(4) In reversible reactions there are probably in general, though not necessarily, two substances, one in each opposing reaction, that functionate alike (as base, acid, or in tendency to form double compounds) toward the catalyzer (acids, bases, salts, enzymes, etc.), although it may not be to the same extent. In reversible reactions, in which the catalyzer forms intermediate compounds and is used up to any appreciable extent in forming the end products, an increase in the concentration of the catalyzer will disturb the equilibrium in the direction which allows the formation of more of that intermediate double compound (catalyzer-end product, $\overset{+}{N}H_3OH$, for example) which has the greatest stability. If the catalyzer is used up appreciably in salt or double-compound formation it is only when the two bases (or acids, etc.) in the opposing reactions have approximately the same affinity constants, and their salts the same dissociation constants and reaction velocities, that the equilibrium point will not be appreciably disturbed by a change in the concentration of the catalyzer. But if the catalyzer is used up to only an inappreciable extent in this formation of salt or double compound, then the equilibrium will not be disturbed appreciably if the catalyzer functionates alike in both opposing reactions.[1] The same reasoning applies to the action of enzymes, alcoholates, etc., when they act as catalyzers through the intermediate reversible formation of double compounds. The equilibrium point for the noncatalyzed reversible reaction between acetone and hydroxylamine in one gram molecule per liter concentrations is different from that of the catalyzed reversible reaction in which the concentrations of

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[1] For a fuller discussion, see Acree and Johnson: THIS JOURNAL, 38, p. 352 *et seq.*

the acetone, hydroxylamine, and hydrochloric acid are also each one gram molecule per liter, and the equilibrium then varies greatly with the variation in the amount of catalyzer, hydrogen ions.[1] In other words, *the third law of catalysis does not hold in this case.*[2] This fact does not conflict with the second law of thermodynamics. It might be thought that the change in equilibrium resulting from the removal of the catalyzer could be used in doing work. But in order to remove the catalyzer the reactions which result when the catalyzer is added must be reversed, and hence the same energy must be applied in doing this as was given up in the direct reactions. That the catalyzer is really the hydrogen ion was shown by the fact that hydrochloric and hydrobromic acids in the same concentrations gave approximately the same equilibrium point. In this reversible reaction the hydroxylamine is the strong base and the acetoxime is the weak base. The greater the concentration of hydrogen ions the greater was the amount of hydroxylamine and hydroxylammonium ions found; in other words, the greater was the amount of the salt of the stronger base. But when an alkali is used as the catalyzer, more of the weak acid, hydroxylamine or acetone, is converted into the salt of the stronger acid, acetoxime. This point was worked out from a theoretical standpoint independently by Acree, Euler, and Abel, and verified by the experimental work of Acree and Johnson.

Unless all reactions are reversible, it is not impossible that a reaction which goes to completion may become a reversible reaction in the presence of a (different) catalyzer, or *vice versa*.

All of the above work makes the writer believe that *a catalyzer may influence the velocity of a reaction physically*,[3] as by condensing the reacting substances on the surfaces of solids, enzymes, etc., and hence increasing the effective concentrations, or by imparting energy to, or removing it from, the system. *A catalyzer (pure or pseudo) may change the velocity of a reaction chemically* by altering the concentration of some substance taking part in the reaction, or by forming some new substance which yields the same end products, or catalyzer-end products. In some cases certain side reactions may be developed or suppressed by the addition or removal of the catalyzer.

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[1] See also Bodenstein and Dietz: Z. Elek. Chem., **12**, 605; Dietz: Dissertation Leipzig, 1907.

[2] Acree and Johnson: This Journal, **38**, 348 *et seq.*

[3] See Bodenstein and coworkers: Z. physik. Chem., **46**, 725; **49**, 41; **53**, 166; **60**, 1, 46. Rowe: *Ibid.*, **59**, 41. Stock, Gomalka, and Heynemann: Ber. d. Chem. Ges., **40**, 532. Stock and Bodenstein: *Ibid.*, **40**, 570. Bodenstein and Dietz: Z. Elek. Chem., **12**, 605; and Dietz: Dissertation, Leipzig, 1907.

JOHNS HOPKINS UNIVERSITY,
Dec. 1, 1907.

REVIEWS.

ELECTRONS, OR THE NATURE AND PROPERTIES OF NEGATIVE ELECTRICITY. By SIR OLIVER LODGE, F.R.S. London: George Bell & Sons. 1906. pp. 230. Price, $2.00.

This book will be welcomed for many reasons, and especially because it comes from the pen of Sir Oliver Lodge. Whatever Lodge discusses in a semipopular style is so well done that it cannot fail to attract the attention of the intelligent, even if they are not specialists.

The present book is the outgrowth of a lecture delivered before the Institution of Electrical Engineers. It "is intended throughout for students of general physics, and in places for specialists," says the author, "but most of it may be taken as an exposition of a subject of inevitable interest to all educated men."

The problems discussed in this work are among the most fundamental with which men of science are concerned, and the experimental work described, especially that of J. J. Thomson, is some of the most brilliant that has ever been carried out in the domain of physics. A glance at some of the chapter headings will show the scope of the book: Properties of an Electric Charge; Electric Inertia; Foreshadowing of the Electron; Ionization of Gases; Determination of the Mass of the Electron; Increase of Inertia Due to Very Rapid Motion; Justification for Electric Theory of Inertia; Electric and Magnetic Deflection Method for Measuring Velocity and Mass of the Particles in Compound Rays; Electric View of Matter; Further Considerations Regarding the Structure of an Atom; Summary of Other Consequences of Electron Theory; Difficulties Connected with the Electric Theory of Matter, Etc.

It will be seen from the above that the book covers just that field with which every man of science, no matter what his special line may be, must become more or less familiar. The treatment is characteristically clear, and not so technical as to exclude it from all but the trained physicist. Any one with a good general knowledge of elementary physics can read the work, and read it with sufficient ease to enjoy it. It is fortunate that a man of the high type of Lodge does not think it an unworthy task to present such matters in a form which is accessible to the intelligent nonspecialist.

H. C. J.

LES NOUVEAUTÉS CHIMIQUES POUR 1907. NOUVEAUX APPAREILS DE RECHERCHES APPLIQUÉES À LA SCIENCE ET À L'INDUSTRIE. Par CAMILLE POULENC, DOCTEUR ES SCIENCES. Avec 196 figures intercalées dans le texte. Paris: Librarie J B. Baillière et Fils; Établissements Poulenc Frères. 1907. pp. xi+347. Price, 4 fr.

The author has followed, in this volume of the "Nouveautés Chimiques," the same general plan as in preceding years. He has collected, from the different scientific journals, brief descriptions of new forms of apparatus which are of interest to chemists. Chapter I. deals with physical, Chapter II. with purely chemical, Chapter III. with electrical, Chapter IV. with analytical, and Chapter V. with bacteriological apparatus, and the laboratory worker may well obtain useful suggestions by looking through this book.

PRACTICAL TEST-BOOK OF CHEMISTRY. By JOHN DABNEY PALMER, M.A., M.D First edition. New York: John Wiley & Sons. Price, $1.00.

This is a collection of qualitative tests for showing the presence of various chemical compounds in drugs and medicines. It is divided into "Specific Tests" and "Tests of Purity," and is intended for physicians and pharmacists. 133 pages are filled with specific tests for 162 substances; for some of these the compiler has collected a large number of tests which are given without indication of relative value or reliability; there are 23 tests for acetanilide, 37 for albumen in urine. Fifty pages are given to tests of purity of chemicals, drugs, canned vegetables, etc.

E. R.

A LABORATORY OUTLINE OF GENERAL CHEMISTRY. By ALEXANDER SMITH, Professor of Chemistry in the University of Chicago. Third edition. Revised in collaboration with WILLIAM J. HALE, Instructor in General Chemistry in the University of Michigan. New York: Century Co. 1907. pp. 136.

This is an excellent manual, and with the exception of a few experiments could be used with any text-book; to obtain the best results, however, it should be used in connection with Professor Smith's "Introduction to General Inorganic

Chemistry," to which reference is constantly made in the text. Three editions and two reprints of this manual since its appearance, in 1899, indicate that it is liked. E. R.

ELEMENTARY PRACTICAL CHEMISTRY. PART I. GENERAL CHEMISTRY. By FRANK CLOWES, D.Sc., Lond., Emeritus Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., Head of the Chemical Department in the Southwestern Polytechnic, Chelsea. Fifth edition. London: J. & A. Churchill; Philadelphia: P. Blakiston's Son & Co. pp. 198. Price, $1.00.

A notice of Part II. of this book appeared in THIS JOURNAL, Vol. 38, p. 251. Part I. is a handy combined text-book and laboratory manual for the use of secondary schools, in which the text-book part is condensed to brief paragraphs, liberally illustrated by laboratory experiments. A lecture course is supposed to parallel the work.

In secondary schools little time can be given to the study of science. The problem is how to use this time to best advantage. The authors offer one of the best solutions of this problem in the book reviewed, giving nearly all the time to laboratory experiment, which is just the training the pupil needs. E. R.

BEET SUGAR MANUFACTURE AND REFINING. Vol. II: Evaporation, Graining and Factory Control. By LEWIS S. WARE. New York: John Wiley & Sons. 1907. Price, $5.00.

This volume completes the most comprehensive treatise on beet sugar manufacture in the English language. Its forty and odd chapters are grouped under the following headings: Evaporation, Manufacture of Raw Sugar, Working After-products, Manufacture of White Sugar, Utilizaton of Residues, Steam Economy, and Practical Work of a Beet Sugar Factory. To this are added numerous tables, largely of Claassen's compilation, and a fair index. The second volume follows the plan of the first, being a well arranged selection of the best foreign literature. It is very well illustrated and gives copious references to the original authorities.

The reviewer regrets that he is again obliged to call attention to the poor English and unsatisfactory translation evident in many places, and especially deplorable in a work of such importance and general excellence in most details of text and typography.

"Tramp" appears in several places for "trap;" "schema," which has a quite different meaning in English, is used for "scheme" (diagram). It is doubtful whether the average technical man would know what is meant by the French "ruissellment," albeit "rendement" and "entrainment" are well-recognized terms in the industry. Much worse is the use of "sheet iron" for "boiler iron."

Perhaps the most glaring instance of all is the table on p. 639, apparently translated from the German of Claassen. Statements such as "cast iron tube, riveted and enameled," "soldered, forged-iron boiler tube," etc., are not only mistranslated and badly rendered but are senseless to the engineer.

Other cases, such as "mushrooms" for "fungi," could be cited. The reviewer knows too well, from his own experience, how easily such slips are made, especially in translations; still it is regrettable that the editing could not have been better in a work of this importance. It is hoped that such blemishes can be removed in a later edition. GEO. W. ROLFE.

TENTH ANNUAL CONVENTION OF ASSOCIATION OF STATE AND NATIONAL FOOD AND DAIRY DEPARTMENTS. New York: John Wiley & Sons. 1906. pp. vi + 349. Price, $3.00.

This publication is of unusual interest in connection with the literature of food legislation and of the manufacture and sale of foods. The proceedings are given in full and include reports and discussions of representatives of the federal and state officers charged with the enforcement of food laws, as well as addresses of manufacturers and dealers in foods. Aside from a record of the resolutions adopted by the Association and the reports of committees, the publication contains the full text of twenty-two addresses on miscellaneous food topics and on the federal food laws and the regulations adopted for their enforcement. The publication is well arranged and has a comprehensive general index. W. D. BIGELOW.

CHEMICAL REAGENTS. THEIR PURITY AND TESTS. A New and Improved Text Based on and Replacing the Latest Edition of Krauch's "Die Prüfung dea chemischen Reagentien auf Reinheit." By E. MERCK. Authorized translation by Henry Schenk, A.B. (Harvard). New York: D. Van Nostrand Co. 1907. 250 pp. Price, $1.50.

This volume gives the characteristics and constants of more than six hundred chemical reagents with well-chosen tests of purity for each.

The former editions of Dr. Krauch's work were well received, and the present translation of the enlarged and revised edition should be within reach of every working chemist. E. R.

GLUES AND GELATINE. A PRACTICAL TREATISE ON THE METHODS OF TESTING AND USE. BY R. LIVINGSTON FERNBACH.

Referring to a review of the book bearing the above title which appeared in the September number of this Journal, the Editor desires to say that the article was in no sense an expression of his own personal views, and that he is not in a position to pass upon the merits of the work. So far as the article in question may have appeared to be unduly harsh, the Editor hereby expresses his regret.

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AMERICAN

CHEMICAL JOURNAL

THE EFFECT OF ONE SALT ON THE HYDRATING POWER OF ANOTHER SALT PRESENT IN THE SAME SOLUTION.

[TWENTIETH COMMUNICATION.]

BY HARRY C. JONES AND CHARLES M. STINE.

Six independent lines of evidence, all pointing to the existence of hydrates in aqueous solutions, having been established, it seemed desirable to attempt to determine, if possible, the effect of one salt with hydrating power upon the hydrates formed by a second salt in the same solution; also the effect of a salt with very small hydrating power on the hydrates formed by another salt. When both salts possess the power of forming hydrates in single solution, the amounts of water taken up by the salts at the same concentrations may be the same, or may vary within wide limits. We proposed to study binary mixtures in which both conditions are illustrated.

Since we desired to calculate, as accurately as possible, the approximate composition of the hydrates formed in the mixtures, it was necessary to obtain data for the freezing points, conductivities, and number of grams of solvent in a liter of solution of the various salts employed. In order that we might have the data for the exact normalities of the solutions which we mixed, it seemed advisable to make the necessary measurements in the single solutions, rather than to attempt to interpolate from data previously obtained.

CONDUCTIVITY CALCULATIONS.

It is well known that when two or more electrolytes are present in the same solution, the conductivity of this solution is not, in general, equal to the sum of the conductivities which these electrolytes have in separate solutions of the same normality as that which these salts may be assumed to have in the mixture; but that the conductivity of the mixture is generally less than this sum. If the solutions are isohydric,[1] that is, if the component solutions possess a common ion in equal concentration, then the simplest condition exists between the conductivities of the single solutions and that of the mixture. This latter condition exists when

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2},$$

in which α_1 is the dissociation of one of the electrolytes at the dilution v_1, and α_2 is the dissociation of the other electrolyte at the dilution v_2. Such solutions can be mixed in any proportion without altering their dissociation, and, hence, the conductivity of the mixture is the mean of the conductivities of the component solutions and can, therefore, be calculated according to the equation

$$k = \frac{k_1P + k_2P'}{P + P'},$$

in which k_1 and k_2 are the conductivities, and P and P' the proportions of the component solutions.

Unfortuately, we have to deal with no such simple relations as these in the mixtures with which we worked.

In our work, the viscosity of the mixtures differs considerably, in many cases, from that of the single solutions assumed to have the same normality. This would involve changes in friction in the movement of the ions. Also, the amount of water combined as hydrate, *i. e.*, the dimensions of the atmosphere about the ion, continually changed from one normality to another. This involved a varying degree of freedom of movement of the ions. Again, the variation in the number of particles present, ions and molecules, must involve continual variation in the amount of friction between the ions. As a comparatively short, and at the same time sufficiently accurate, method, we have adopted the following in apportioning the diminution in conductivity to the constituent salts: Since we have dealt in every case with mixtures in which the two electrolytes have a common ion, we have based the method on the number of this common ion yielded by the constituent salts in separate solutions at the same normality. By the same normality, we mean that if equal volumes of two solutions are mixed, and any diminution in volume which may take place upon mixing is compensated for by the addition of pure solvent, then the normality of each solution in the mixture may be assumed to be exactly half of that of the constituent solutions. If suppression of the ionization is dependent upon the common ion, then it will be inversely as the number of this common ion furnished by each of the salts in a mixture. This number was obtained thus: The figure representing the normality of the individual solutions, multiplied by the value of α for the solution at the normality in question, would give the gram atomic weight of the common ion. Suppose the case to be one where a solution of potassium chloride has been added to an equal volume of a solution of calcium chloride. It being assumed that calcium chloride dissociates into

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[1] Arrhenius: Wied. Ann., **30**, 51 (1887); Z. physik. Chem., **2**, 284 (1888).

$$\overset{++}{\mathrm{Ca}},\ \text{and}\ \overset{-}{\mathrm{Cl}},\ \overset{-}{\mathrm{Cl}},$$

the figure representing the gram atomic weight of the common ion would have to be doubled for a ternary electrolyte, such as calcium chloride. Since two chlorine ions are required to re-form a molecule of calcium chloride, the figure expressing the number of chlorine ions driven back, in the case of calcium chloride, must be divided by two, in order to get the relative number of molecules of calcium chloride re-formed.

Let us take the values of Λ_∞ as expressing the molecular conductivity of the completely dissociated molecules of the various salts. If the figures for the relative numbers of molecules of the two salts re-formed be multiplied by the proper value of Λ_∞, we shall then have the relative losses in conductivity. From this the absolute losses are readily obtained. An example may suffice to make this clear: Take the case of the mixture of equal volumes of a solution of 1.8 N calcium chloride and of 1.7 N potassium chloride. The resulting solution, any diminution of volume having been compensated for, will consist of 0.9 N calcium chloride and 0.85 N potassium chloride. The dissociation of a 0.9 N solution of the specimen of calcium chloride employed was found, by conductivity measurements, to be 53.2 per cent, of 0.85 N potassium chloride, 83.2 per cent. Doubling the value of α in the case of calcium chloride and multiplying by the normality, we get 0.9576. Similarly, for potassium chloride, 0.7068. These represent the relative numbers of chlorine ions which would be furnished by each salt in the mixture if no suppression of the ionization took place upon mixing. That is, if driving back occurs, according to the law of mass action, 707 chlorine ions should be driven back to re-form calcium chloride to 958 for potassium chloride. But since it requires two ions of chlorine to re-form each molecule of calcium chloride, only 354 molecules of calcium chloride will be re-formed to every 958 molecules of potassium chloride. Multiplying these values by Λ_∞ for calcium chloride and potassium chloride, respectively, we get 5222, approximately, for calcium chloride and 7695 for potassium chloride. These values represent the relative losses in conductivity upon mixing. From this the decrease in conductivity can be apportioned between the two salts.

All conductivity measurements are given as specific conductivities in the mixtures. The units employed are reciprocal centimeter ohms. For purposes of comparison with the previous work upon the "hydrate theory" our units may be transformed by dividing Λ_v by 1.069.

The approximate composition of the hydrates in the *single* solutions was calculated by the method previously employed by Jones and his coworkers.

EXPERIMENTAL WORK.

Freezing Point.—The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing temperature being determined by means of alcohol thermometers. These temperatures could not be measured more closely than 0°.5. For the more dilute solutions freezing mixtures of ice and sodium chloride, or ice and crystallized calcium chloride, were employed. The temperature was read by means of Beckmann thermometers, covering ranges of 6°, 12°, and 25°, respectively. When the more concentrated solutions were frozen, they were removed from the bath of solid carbon dioxide and alcohol as soon as ice began to separate, in order that they might not be surrounded by the very cold freezing mixture while temperature equilibrium was being established. The necessary correction for the separation of ice and consequent increase in concentration was introduced in every instance. The separation of some of the dissolved substance was readily ascertained by the grit or sandlike character of the solid that separated, which was easily detected. Since it was found that, for the volume of liquid employed in the freezing point tube (about twenty-five cubic centimeters), a freezing point determination made with a large undercooling and, consequently, a copious separation of ice gave a slightly different result from one where the undercooling was less, care was taken, in the freezing point determinations of both the pure solvent and the solutions, to keep the undercooling nearly the same throughout—about a degree. This necessitated innoculating the solution, in nearly every case, with an exceedingly minute particle of the solid phase of the solvent.

CONDUCTIVITY.

Conductivities were measured by the method of Kohlrausch.

The resistance coils, manufactured by Leeds & Co., were tested and found in no case to involve a greater error than 0.04 per cent.

The dilute solutions were measured in conductivity cells of the form employed by Jones and Bingham,[1] the tubes carrying the platinum electrodes being sealed into both the upper and lower walls of the stopper. For the more concentrated solutions, cells of the type used by Jones and Getman[2] were employed. The electrodes were treated in the usual manner (coated with platinum black, etc.), in order to obtain a sharper tone minimum or point of silence in the readings.

The cells for the more dilute solutions were standardized by determining the cell constant by means of N/50 potassium chloride. The value $k = 0.0015133$ was taken as the conductivity of N/50 potassium chloride. For the more concentrated solutions, the cell constants were determined with a N/2 solution of potassium chloride, for which $k = 0.03365$ at 0°.[3] The potassium chloride employed in determining cell constants was recrystallized five times, the last two times from conductivity water, and was free from all appreciable impurities. The cell constants were frequently redetermined, but very little change in them was noted from time to time. The cells were filled with distilled water when not in use, and were always carefully cleansed, dried, and rinsed with the new solution when a change in solutions was made. All conductivities were measured at 0°. The temperature of the zero bath was always within a tenth of a degree of 0°, as determined by an accurately standardized thermometer. All conductivity measurements are the average of four readings with different resistances in circuit.

The water used in this work was purified as in former work.

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. Especially is this the case at the concentrations with which we dealt, since the values of Λ_∞, which we used in our mixtures, were determined for each salt by diluting the single solution to a maximum value of Λ_v. This is, obviously, a source of additional error, for the conductivity of the ions resulting from a completely dissociated molecule in a very dilute solution must be different from the conductivity of those ions in a more concentrated solution. In the more dilute solution a larger atmosphere of the solvent is attached to the ions, and this must be dragged along by them. There is present a much smaller number of particles of salt (ions or molecules) in the dilute than in the more concentrated solution. Consequently, the friction between the ions in their movements must be different. The viscosity of the solutions in which Λ_∞ can be determined is very much less than the viscosity of the solutions at the concentrations employed. These are all important factors which affect the conductivity of any dissolved substance. The method is, however, an approximate one for measuring such dissociations, and is the best available at present. All that can be said is that it probably gives values of the right order of magnitude.

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[1] This Journal, **34**, 481 (1905).

[2] Z. physik. Chem., **46**, 254 (1903).

[3] These values are calculated from the results of Jones and West. See This Journal, **34**, 381 (1905).

CALCIUM CHLORIDE.

A strong solution of calcium chloride was prepared and standardized. All solutions were made by diluting the calculated amount of the original solution to the required volume.

Table I.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.3	1°.517	5.056	1.4	10°.05	7.18
0.5	2°.672	5.344	1.55	11°.58	7.47
0.6	3°.270	5.450	1.755	14°.33	8.16
0.7	4°.065	5.807	1.88	14°.69	8.16
0.9	5°.422	6.024	2.2	21°.07	9.58
1.0	6°.410	6.310	2.7	30°.25	11.20
1.1	7°.080	6.436	3.1	39°.5	12.74
1.35	9°.362	6.934	3.5106	49°.5?	14.10?

In this table, as elsewhere where they occur, m is the concentration in terms of gram molecules per liter; Δ, the observed freezing point lowering, corrected for the separation of ice; and Δ/m, the molecular lowering of the freezing point.

Table II.—Conductivity Measurements.

Λ_∞ 0° = 147.52.[1]

m.	V.	k.	Λ_v.	α.
0.3	3.333	0.028044	93.5	0.634
0.5	2.000	0.043801	87.6	0.594
0.6	1.6666	0.050268	83.8	0.568
0.7	1.4285	0.057555	82.2	0.557
0.9	1.1111	0.070601	78.4	0.532
1.0	1.000	0.075540	75.5	0.512
1.1	0.909	0.081573	74.1	0.502
1.35	0.7407	0.092860	68.8	0.466
1.4	0.7143	0.09396	67.1	0.455
1.55	0.6453	0.099184	64.0	0.434
1.755	0.5698	0.10723	61.1	0.414
1.8	0.5555	0.107267	59.8	0.405
2.2	0.4545	0.115876	52.7	0.357
2.7	0.3704	0.7757	43.6	0.296
3.1	0.3226	0.11410	36.8	0.250
3.5106	0.2849	0.10710	30.5	0.207

In this table, as elsewhere throughout this paper, m is the concentration, in terms of gram molecules per liter; V is the number of liters that contain a gram molecule of the dissolved substance; k is the specific conductivity, and is equal to

$$\frac{0.001069\mu_v}{v};$$

Λ_v is the molecular conductivity at 0°, and is equal to $1000 \times V \times k$; α is the percentage of dissociation, and is equal to Λ_v/Λ_∞.

Table III.—Weight-Normal Corrections, or Number of Grams of Solvent in 1000 Cubic Centimeters of Solution.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. per cent.
0.3	51.270	1.665	49.605	0.8
0.5	52.2608	2.775	49.4858	1.0
0.6	52.7437	3.33	49.4137	1.2
0.7	53.1162	3.885	49.2312	1.5
0.9	53.9816	4.995	48.9866	2.0
1.0	54.326	5.55	48.776	2.4

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[1] Calculated from the value given by Jones and Bassett: This Journal, **33**, 547 (1905).

Table III—(*Continued*).

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
1.1	54.772	6.105	48.667	2.7
1.35	55.9435	7.4925	48.451	3.1
1.4	56.115	7.770	48.345	3.3
1.55	56.6562	8.6025	48.0537	3.9
1.755	57.7040	9.7402	47.9638	4.1
1.8	28.900	4.995	23.905	4.4
2.2	29.650	6.105	23.545	5.8
2.7	30.682	7.492	23.190	7.2
3.1	31.461	8.602	22.859	8.6
3.5106	32.187	9.720	22.467	10.1

In these tables of weight-normal corrections, m has the usual significance; $W_{Sol.}$ is the weight of twenty-five or of fifty cubic centimeters of the solution; W_{Salt} is the weight of salt contained in this volume of the solution; W_{H_2O} is the weight of water in this volume of solution, equal to $W_{Sol.} - W_{Salt}$; "Correction, per cent," is the percentage of correction to be applied in order to refer measurements to a thousand grams of solvent. These are not specific gravity measurements made in pycnometers, and we therefore give the correction percentage only to the first decimal.

In the following tables, as in all other tables of the hydrates formed in the single solutions, m has the usual significance; α is the percentage of dissociation; L is the theoretical molecular lowering of the freezing point referred to a thousand grams of the solvent; Δ/m, the molecular lowering found experimentally; L', the molecular lowering; M, the number of gram molecules of water in combination, both being referred to a thousand grams of solvent—

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18}.$$

H is the number of molecules of water in combination with one molecule of the salt, at the concentration in question, if a liter of the solution at that concentration contained a thousand grams of water. It equals M/m.

Table IV.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L'.*	*M.*	*H.*
0.3	0.634	4.22	5.06	5.02	8.8	29.4
0.5	0.594	4.09	5.34	5.29	12.6	25.2
0.6	0.568	3.97	5.45	5.39	14.6	24.3
0.7	0.557	3.93	5.81	5.72	17.4	24.8
0.9	0.532	3.84	6.02	5.90	19.4	21.6
1.0	0.512	3.76	6.31	6.16	21.6	21.6
1.1	0.502	3.73	6.44	6.26	22.4	20.4
1.35	0.466	3.59	6.93	6.72	25.9	19.2
1.4	0.455	3.55	7.18	6.94	27.2	19.4
1.55	0.434	3.47	7.47	7.18	28.7	18.5
1.755	0.414	3.40	8.16	7.83	31.4	17.9
1.8	0.405	3.37	8.16	7.80	31.6	17.5
2.2	0.357	3.19	9.58	9.03	35.9	16.3
2.7	0.296	2.96	11.20	10.39	39.7	14.7
3.1	0.250	2.79	12.74	11.65	43.6	14.1
3.5106	0.207	2.63	14.10	12.68	46.5	13.2

Since we wished to investigate the effect of the presence of a salt with little hydrating power upon a salt with considerable hydrating power, potassium chloride was added to calcium chloride. The data for the various solutions of potassium chloride alone are next given.

POTASSIUM CHLORIDE.

Table V.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.45	1°.52	3.35	1.2972	4°.48	3.45
0.65	2°.24	3.45	1.3	4°.49	3.46
0.85	2°.91	3.43	1.7	5°.93	3.49
0.90	3°.08	3.42	2.1	7°.43	3.54
1.05	3°.58	3.41	2.5945	9°.29	3.58

Table VI.—Conductivity Measurements.

Λ_∞ 0° = 80.33.[1]

m.	*V.*	*k.*	Λ_v.	*α.*
0.45	2.222	0.030332	67.4	0.839
0.65	1.538	0.043608	67.1	0.835
0.85	1.1765	0.056804	66.8	0.832
0.90	1.1111	0.058717	65.2	0.812

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[1] Calculated from the value given by Jones and West: THIS JOURNAL, 34, 381 (1905).

Table VI—(Continued).

m.	*V.*	*k.*	Λ_v.	α.
1.05	0.9523	0.068969	65.7	0.818
1.2972	0.7709	0.083948	64.7	0.805
1.3	0.7792	0.084118	64.7	0.805
1.7	0.5882	0.109202	64.2	0.800
2.1	0.4762	0.133785	63.7	0.793
2.5945	0.3854	0.163207	62.8	0.782

Table VII.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. per cent.
0.45	8.0042	0.26353	7.74067	1.4
0.65	8.0735	0.38066	7.69284	2.0
0.85	8.1443	0.49654	7.64766	2.6
0.90	25.9936	1.6785	24.3151	2.7
1.05	8.2169	0.61492	7.60198	3.2
1.3	26.5127	2.4245	24.0882	3.7
1.7	26.928	3.1705	23.7575	5.0
2.1	27.4457	3.9165	23.5292	5.9
2.5945	28.0254	4.8385	23.1869	7.3

Table VIII.—Hydrates.

m.	α.	*L.*	Δ/m.	*L'*	*M.*	*H.*
0.45	0.839	3.42	3.35	3.30	....	....
0.65	0.835	3.41	3.45	3.38	....	....
0.85	0.832	3.41	3.43	3.34	....	....
0.90	0.812	3.37	3.42	3.32	....	....
1.05	0.818	3.38	3.41	3.40	....	....
1.2972	0.805	3.36	3.45	3.33	....	....
1.3	0.805	3.36	3.46	3.33	....	....
1.7	0.800	3.35	3.49	3.31	....	....
2.1	0.793	3.34	3.54	3.33	....	....
2.5945	0.782	3.32	3.58	3.32	....	....

There is evidently no hydrating power.

MIXTURE OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE.

Table IX.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
1.0 $CaCl_2$	1	4°.413	2.7 $CaCl_2$	1	15°.00
0.9 KCl	1		2.5945 KCl	1	
1.4 $CaCl_2$	1	6°.625	3.1 $CaCl_2$	1	16°.50
1.3 KCl	1		2.5945 KCl	1	
1.8 $CaCl_2$	1	9°.17	3.5106 $CaCl_2$	1	18°.0
1.7 KCl	1		2.5945 KCl	1	
2.2 $CaCl_2$	1	12°.01			
2.1 KCl	1				

Table X.—Conductivity Measurements.

m.	P.	m_c.	V_c.	k_u.	k.	D.	k_c.	Λ_v.	α.
1.0 $CaCl_2$	1	0.5	2.0000	0.069977.	0.043801	0.004158	0.048890	84.6	0.573
0.9 KCl	1	0.45	2.2220		0.030332		0.027687	61.5	0.766
1.4 $CaCl_2$	1	0.7	1.4285	0.093713	0.057555	0.00745	0.054653	78.1	0.529
1.3 KCl	1	0.65	1.5380		0.043608		0.039060	60.0	0.748
1.8 $CaCl_2$	1	0.9	1.1111	0.114096	0.070601	0.013309	0.065221	72.5	0.491
1.7 KCl	1	0.85	1.1765		0.056804		0.048875	56.5	0.716
2.2 $CaCl_2$	1	1.1	0.9090	0.13081	0.081573	0.01973	0.073353	66.7	0.452
2.1 KCl	1	1.05	0.9523		0.068969		0.057459	54.7	0.681
2.7 $CaCl_2$	1	1.35	0.7407	0.14805	0.092860	0.02876	0.080410	59.6	0.404
2.5945 KCl	1	1.2972	0.7709		0.083948		0.067650	52.2	0.649
3.1 $CaCl_2$	1	1.55	0.6451	0.15081	0.099184	0.03232	0.057794	55.4	0.375
2.5945 KCl	1	1.2972	0.7709		0.083948		0.065018	50.1	0.624
3.5106 $CaCl_2$	1	1.755	0.5698	0.15239	0.107230	0.03879	0.091830	52.3	0.355
2.5945 KCl	1	1.2972	0.7709		0.083948		0.060560	46.7	0.581

In Table IX. the column headed P indicates parts by volume of each solution which were mixed; m is the normality of the solutions before mixing. In order that each solution should have exactly one-half the normality after mixing which it had before, the volume of the mixture was brought to exactly twice the volume by the addition of either of the constituent solutions.

In Table X. m is the normality of the solutions mixed. P is the parts by volume of each solution which were mixed. When equal volumes are mixed the resulting normality of each solution is exactly one-half of that of the solutions before mixing. This is given under m_c. V_c is the number of liters of solution that will contain a gram molecular weight of the salt, based on m_c. k_u is the specific conductivity of the mixture. This would be the sum of the conductivities of the component solutions if no suppression of the ionization occurred. k gives the conductivities of the single solutions of each salt at the normality acquired upon mixing. In each case the sum of these two, minus the conductivity of the mixture, k_u, gives the decrease in conductivity due to the driving back of the dissociation of the salts in question. This is given under D. This loss in conductivity is then apportioned to each electrolyte by the method already described, and the resulting conductivities are given under k_c. From this, Λ_v and α are obtained.

Table XI.—Weight-Normal Corrections.

m.	*P.*	$w_{Sol.}$	$w_{Salt.}$	w_{H_2O}.	Correction, per cent.
1.0 $CaCl_2$	1	26.7448	2.22637	24.51843	1.9
0.9 KCl	1				
1.4 $CaCl_2$	1	27.3662	3.1542	22.2120	3.2
1.3 KCl	1				
1.8 $CaCl_2$	1	28.0354	4.0827	23.9527	4.2
1.7 KCl	1				
2.2 $CaCl_2$	1	28.6177	5.0102	23.6075	5.6
2.1 KCl	1				
2.7 $CaCl_2$	1	29.422	6.1655	23.2565	6.9
2.59 KCl	1				
3.1 $CaCl_2$	1	29.8247	6.7205	23.1042	7.6
2.59 KCl	1				
3.51 $CaCl_2$	1	30.2118	7.2793	22.9235	8.3
2.59 KCl	1				

Proceeding upon the tentative hypothesis that the calcium chloride forms the same hydrates in the presence of a salt with no hydrating power that it forms in separate solution, the values in Tables XII. and XIII. were calculated.

Table XII.—Calcium Chloride in the Mixture.

m.	*P.*	*mc.*	*α.*	*L.*	*I.*
1.0 $CaCl_2$	1	0.5	0.573	3.992	2.034
0.9 KCl	1				
1.4 $CaCl_2$	1	0.7	0.529	3.829	2.769
1.3 KCl	1				
1.8 $CaCl_2$	1	0.9	0.491	3.687	3.464
1.7 KCl	1				
2.2 $CaCl_2$	1	1.1	0.452	3.541	4.126
2.1 KCl	1				
2.7 $CaCl_2$	1	1.35	0.404	3.362	4.880
2.59 KCl	1				
3.1 $CaCl_2$	1	1.55	0.375	3.256	5.462
2.59 KCl	1				
3.51 $CaCl_2$	1	1.7553	0.355	3.179	6.084
2.59 KCl	1				

α is the dissociation of the calcium chloride in the mixture. L is the freezing point lowering calculated from the formula $(1.86 \times 2\alpha) + 1.86$. I is the freezing point lowering, corrected to one thousand grams of solvent, which the salt would give if there were *no* hydration.

Table XIII.

m.	*P.*	*mc.*	*α.*	Δ.	W_{H_2O}.	Correction, per cent.	*I.*
1.0 $CaCl_2$	1	0.45	0.766	1.478	753.7	24.6	1.961
0.9 KCl	1						
1.4 $CaCl_2$	1	0.65	0.748	2.113	655.9	34.4	3.222
1.3 KCl	1						
1.8 $CaCl_2$	1	0.85	0.716	2.712	608.2	39.2	4.454
1.7 KCl	1						
2.2 $CaCl_2$	1	1.05	0.681	3.283	538.5	46.2	6.097
2.1 KCl	1						
2.7 $CaCl_2$	1	1.2972	0.649	3.068	464.7	53.5	8.564
2.59 KCl	1						
3.1 $CaCl_2$	1	1.2972	0.624	3.021	408.0	59.2	9.605
2.59 KCl	1						
3.51 $CaCl_2$	1	1.2972	0.581	2.941	340.5	66.0	11.20
2.59 KCl	1						

α is the dissociation of the potassium chloride in the mixture; Δ is the freezing point lowering deduced from $[(1.86 \times \alpha) + 1.86]m_c$; W_{H_2O} is the weight of water acting as solvent towards the potassium chloride, deduced from $L : L :: X : 1000$, which gives the amount of water taken up by the calcium chloride in the formation of hydrates when it alone is present in solution, and from the weight-normal correction for the mixture; I is the ideal lowering which the potassium chloride would give if the calcium chloride formed the same hydrates in the mixture that it forms when alone in solution.

Table XIV.—Comparison of Lowerings due to Hydration in Separate Solution of Calcium Chloride and in the Mixture.

m.	*mc.*	Δ_c.	I_c.	Diff$_c$.	Δ.	*I.*	Diff.
1.0 $CaCl_2$ 0.9 KCl	0.5	4.413	3.995	0°.418	2.672	2.066	0°.606
1.4 $CaCl_2$ 1.3 KCl	0.7	6.625	5.991	0°.634	4.004	2.750	1°.25
1.8 $CaCl_2$ 1.7 KCl	0.9	9.170	7.918	1°.252	5.314	3.455	1°.859
2.2 $CaCl_2$ 2.1 KCl	1.1	12.01	10.223	1°.782	6.896	4.100	2°.799
2.7 $CaCl_2$ 2.59 KCl	1.35	15.0	13.442	1°.558	9.072	4.851	4°.221
3.1 $CaCl_2$ 2.59 KCl	1.55	16.5	15.067	1°.433	11.13	5.385	5°.745
3.51 $CaCl_2$ 2.59 KCl	1.7553	18.0	17.288	0°.712	14.10	5.970	8°.130

(*P* = 1 in every case.)

Δ_c is the lowering found experimentally for the mixture. I_c is the sum of I in Tables XII. and XIII. Diff$_c$ = $\Delta_c - I_c$ = lowering due to hydration. Δ is the lowering found experimentally for calcium chloride, corrected to one thousand grams of solvent. I is the lowering the calcium chloride should have given in 1000 grams of solvent, if there were no hydration. Evidently, Diff$_c$. and Diff. should be identical if there were no change in hydration. Such is not the case. Consequently, the basis assumed for the calculation of I for potassium chloride in the mixture is incorrect, since it depends upon a knowledge of the amount of water eliminated from the sphere of action as solvent by the hydration of the calcium chloride. It, therefore, becomes necessary to derive a formula for the calculation of the hydration of the calcium chloride in the mixture.

FORMULA FOR CALCULATING LOWERING DUE TO HYDRATION, IN A BINARY MIXTURE OF ELECTROLYTES, WHERE ONE SALT HAS NO HYDRATING POWER.

Let X degrees equal lowering due to hydration of the salt with hydrating power in the mixture.

I = theoretical lowering which the salt with hydrating power should give in the mixture in question, at the corrected dissociation, if there were no hydration.

V = number of liters that contain a gram molecule of the salt with hydrating power, at the normality it has in the mixture.

Then,

$$(X + I)v = \Delta / m.$$

s = correction to 1000 grams of solvent, necessary in the mixture.

$$(X + I)v - (X + I)vs = L'.$$

X' = amount of water acting as solvent towards the salt with *no* hydrating power.

$$L : L' :: X' : 1000.$$

L = $(1.86 \times 2\alpha) + 1.86$, in a ternary electrolyte, where a represents the corrected dissociation of the salt with hydrating power *in the mixture.*

$$\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs}\ 1000 = X'.$$

But taking into account the weight-normal correction also, in the mixture in question, the above becomes

$$\left[\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs}\ 1000\right] - 10\,S =$$

amount of water actually acting as solvent towards the salt with *no* hydrating power. Putting this into the form of a percentage correction,

$$\frac{(1.86 \times 2\alpha) + 1.86}{(X + I)v - (X + I)vs} - \frac{S}{10} =$$

the per cent by which I for the salt with little, or no, hydrating power must be divided.

Let α' = the corrected dissociation in the mixture of the salt with no hydrating power,

$$[(1.86 \times \alpha') + 1.86]m =$$

lowering it would give in 1000 grams of solvent, if it is a binary electrolyte. m is the normality of the salt with no hydrating power.

Then,

$$\frac{1.86m(\alpha' + 1)}{\dfrac{1.86(2\alpha + 1)}{(X + I)(v - vs)} - \dfrac{S}{100}} + X + I =$$

lowering found experimentally for the mixture. From this expression the value of X may be derived.

By means of this formula the value of X has been calculated for the various concentrations employed in the mixture of calcium chloride and potassium chloride, and the results are given in Table XV. The significance of the abbreviations has already been given in connection with the preceding tables.

In order to compare the hydrates formed by calcium chloride in separate solution with those which it forms in the mixture with potassium chloride, the values of M are plotted against the concentrations as abscissas in Fig. I.

It is seen that while the value of M increases with increase in concentration, in general, in the mixture as in separate solution, M is less in the mixture than in separate solution of calcium chloride. This is just what we should expect, since there is less water present as solvent in the mixture of calcium chloride and potassium chloride, at any given concentration of the calcium chloride, than there is at the same

Table XV.—Hydration of $CaCl_2$ in Mixture.

m.	P.	Mc.	α.	L.	I.	X.	Δ/m.	L′.	M.	H.
1.0 $CaCl_2$ 0.9 KCl	1 1	0.5	0.573	3.92	2.034	0.456	4.981	4.886	10.2	23.8
1.4 $CaCl_2$ 1.3 KCl	1 1	0.7	0.529	3.829	2.769	0.909	5.254	5.086	13.7	19.6
1.8 $CaCl_2$ 1.7 KCl	1 1	0.9	0.491	3.687	3.464	1.537	5.556	5.323	17.1	19.0
2.2 $CaCl_2$ 2.1 KCl	1 1	1.1	0.452	3.541	4.126	2.291	5.834	5.507	19.8	18.0
2.7 $CaCl_2$ 2.59 KCl	1 1	1.35	0.404	3.362	4.88	2.94	5.978	5.387	20.9	15.5
3.1 $CaCl_2$ 2.59 KCl	1 1	1.55	0.375	3.256	5.462	3.601	5.847	5.403	22.1	14.3
3.51 $CaCl_2$ 2.59 KCl	1 1	1.7553	0.355	3.179	6.084	4.32	5.928	5.436	23.1	13.1

concentration of the single solution of calcium chloride. Now it is evident, from previous work, that while the *total number of gram molecules of water combined increases, in general, with increase in concentration, the molecular hydration decreases with increase in concentration.* That is, the amount of water with which a molecule of the calcium chloride or the resulting ions combine depends upon the number of molecules of water present to one molecule of the calcium chloride. If, now,

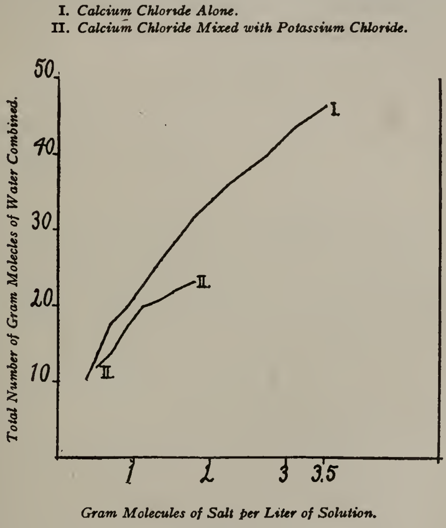


Fig. I.

instead of increasing the number of grams of salt with hydrating power present in a given solution, and thus diminishing the amount of water, we add to the calcium chloride a substance like potassium chloride and then make up to the former volume, it is evident that, there being less water present, the amount of water with which each molecule or ion of calcium chloride will combine will be diminished; that is, the value of M will be diminished.

In order to compare the difference between the amount of water present acting as solvent towards the calcium chloride in the single solution and in the mixture with the difference in the values of M in the two cases, we give in the following table, under D_{H_2O}, the difference between the number of grams of water present as solvent in the separate solution of calcium chloride and in the mixture at the respective concentrations; under D_m, the difference in the values of M for the separate solution of the calcium chloride and in the mixture at the same concentrations.

Table XVI.

m.	D_{H_2O}.	D_m.
0.5	9	2.4
0.7	17	2.8
0.9	22	2.34
1.1	29	2.61
1.35	38	4.99
1.55	38	6.62
1.7553	42	8.36

These results are plotted in curves as Fig. II. For the first four concentrations the values of M decrease by the same amount, since the amount of potassium chloride added is increased as the calcium chloride is increased. Consequently, the curve for the difference in the values of M is approximately parallel to the axis of abscissas (concentration). Referring to Table XV., it will be seen that the difference between successive values of M diminishes with increase in concentration, until finally, in the mixture containing 2.7 N calcium chloride and 2.59 N potassium chloride, M has the value 20.9. The effect of the potassium chloride on the amount of water with which the calcium chloride can combine is such that, although the same amount of potassium chloride is added to the succeeding mixtures, the calcium chloride can increase its water of hydration only slightly, and by a constant difference, with increase in the concentration of the calcium chloride added Consequently, there is increasing deviation, in Fig. I., between the curve representing the value of M for the single solution and that representing M for the mixture. In Fig. II., the difference between the values of M for calcium chloride in the separate solution and in the mixture is approximately proportional to the difference in the amount of water present acting as solvent towards the calcium chloride in the separate solution and in the mixture. This is shown by Curve II.

I. *Difference between Amount of Water Present in the Single Solution of Calcium Chloride and Potassium Chloride.*

II. *Difference between Values of M for Calcium Chloride in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Potassium Chloride.*

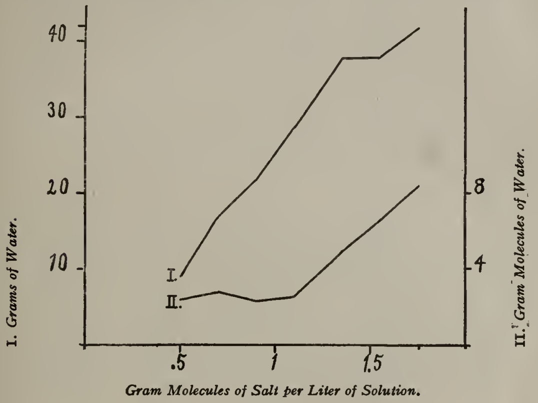


Fig. II.

It must be borne in mind that these results are based on the assumption that calcium chloride breaks down at once into $\overset{++}{\mathrm{Ca}}$, $\overset{-}{\mathrm{Cl}}$, $\overset{-}{\mathrm{Cl}}$; also, that the entire decrease in conductivity upon mixing is due to re-formation of the molecules, whereas a part of the decrease is certainly due to viscosity and friction of the ionic spheres, as already mentioned.

In order to ascertain the effect upon the hydrates formed, a pair of salts, both of which have hydrating power, was next studied.

For this purpose it was considered desirable to investigate, first, a case where both the salts employed have a large hydrating power, and where the hydrating power of the two salts in single solution is of the same order of magnitude. Calcium chloride and magnesium chloride fulfill these conditions.

CALCIUM CHLORIDE.

Table XVII.—Freezing Point Measurements.

m.	Δ.	Δ/*m*.	*m.*	Δ.	Δ/*m*.
0.15	0°.74	4.93	0.85	5°.05	5.94
0.25	1°.265	5.06	1.05	6°.65	6.33
0.35	1°.801	5.15	1.25	8°.41	6.73
0.45	2°.35	5.22	1.45	10°.51	7.25
0.65	3°.55	5.62			

Table XVIII.—Conductivity Measurements.

Λ_∞ 0° = 147.5.

m.	*V.*	*k.*	Λ_v.	*α.*
0.15	6.6666	0.014991	99.9	0.677
0.25	4.0000	0.024073	96.3	0.653
0.35	2.8571	0.032700	93.4	0.633
0.45	2.2222	0.039688	88.2	0.598
0.64	1.538	0.054236	83.4	0.565
0.83	1.1765	0.066903	78.7	0.534
1.05	0.9523	0.078244	74.5	0.505
1.25	0.8000	0.088853	71.1	0.482
1.45	0.6897	0.097385	67.2	0.455

Table XIX.—Weight-Normal Corrections.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.15	25.3227	0.41625	24.90645	0.4
0.25	25.5423	0.69375	24.84855	0.6
0.35	25.8040	0.97125	24.83275	0.7
0.45	26.0110	1.24875	24.76225	1.0
0.65	26.4384	1.80375	24.63465	1.5
0.85	26.8816	2.35875	24.52285	1.9
1.05	27.2846	2.91375	24.37085	2.5
1.25	27.6792	3.46875	24.21045	3.2
1.45	28.1293	4.02375	24.10555	3.6

Table XX.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.15	0.677	4.38	4.93	4.91	6.0	40.2
0.25	0.653	4.29	5.06	5.03	8.2	32.8
0.35	0.633	4.22	5.15	5.11	9.7	27.8
0.45	0.598	4.08	5.22	5.17	11.7	25.9
0.65	0.565	3.96	5.62	5.53	15.7	24.3
0.85	0.534	3.85	5.94	5.83	18.9	22.3
1.05	0.505	3.74	6.33	6.18	21.9	20.9
1.25	0.482	3.65	6.73	6.50	24.3	19.5
1.45	0.455	3.55	7.25	6.99	27.3	18.8

MAGNESIUM CHLORIDE.

Table XXI.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.15	0°.747	4.98	0.85	5°.404	6.36
0.25	1°.306	5.22	1.05	7°.191	6.84
0.35	1°.910	5.46	1.25	9°.236	7.39
0.45	2°.537	5.64	1.45	11°.47	7.91
0.65	3°.854	5.93			

Table XXII.—Conductivity Measurements.

m.	*V.*	*k.*	Λ_v.	*α.*
0.15	6.6666	0.013642	90.9	0.705
0.25	4.0000	0.021529	86.1	0.667
0.35	2.8571	0.02824	80.7	0.625
0.45	2.2222	0.036183	80.4	0.623
0.65	1.538	0.047864	73.6	0.570
0.85	1.1765	0.057606	67.8	0.525
1.05	0.9523	0.066280	63.1	0.489
1.25	0.8000	0.073499	58.8	0.456
1.45	0.6896	0.078040	53.8	0.417

Table XXIII.—Weight-Normal Corrections.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.15	25.2954	0.3572	24.9382	0.2
0.25	25.5072	0.5954	24.9118	0.4
0.35	25.7066	0.8333	24.8731	0.5
0.45	25.8825	1.717	24.8108	0.8
0.65	26.2378	1.5480	24.6898	1.2
0.85	26.6460	2.0243	24.6217	1.5
1.05	27.0011	2.5006	24.5005	2.0
1.25	27.3538	2.9768	24.3770	2.5
1.45	27.7095	3.4532	24.2563	3.0

Table XXIV.—Hydrates.

m.	*α.*	*L.*	$\Delta/m.$	*L′.*	*M.*	*H.*
0.15	0.705	4.48	4.98	4.97	5.5	36.5
0.25	0.667	4.34	5.22	5.20	9.2	36.7
0.35	0.625	4.19	5.46	5.43	12.7	36.3
0.45	0.601	4.10	5.64	5.58	14.9	33.1
0.65	0.570	3.98	5.93	5.86	17.8	27.4
0.85	0.525	3.81	6.36	6.26	21.7	25.6
1.05	0.489	3.68	6.84	6.70	25.1	23.9
1.25	0.456	3.56	7.39	7.20	28.1	22.5
1.45	0.417	3.41	7.91	7.67	30.9	21.3

MIXTURE OF CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE.

Table XXV.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.3 $CaCl_2$	1	1°.553	1.7 $CaCl_2$	1	13°.50
0.3 $MgCl_2$	1		1.7 $MgCl_2$	1	
0.5 $CaCl_2$	1	2°.704	2.1 $CaCl_2$	1	19°.50
0.5 $MgCl_2$	1		2.1 $MgCl_2$	1	
0.7 $CaCl_2$	1	4°.053	2.5 $CaCl_2$	1	27°.25
0.7 $MgCl_2$	1		2.5 $MgCl_2$	1	
0.9 $CaCl_2$	1	5°.543	2.9 $CaCl_2$	1	37°.0
0.9 $MgCl_2$	1		2.9 $MgCl_2$	1	
1.3 $CaCl_2$	1	9°.320			
1.3 $MgCl_2$	1				

Table XXVI.—Conductivity Measurements.

m.	*P.*	m_c.	V_c.	k_u.	*k.*	*D.*	k_c.	Λ_v.	*a.*
0.3 $CaCl_2$	1	0.15	6.6666	0.026923	0.014991	0.001711	0.014062	93.8	0.636
0.3 $MgCl_2$	1	0.15	6.6666		0.013642		0.012861	85.7	0.664
0.5 $CaCl_2$	1	0.25	4.000	0.041214	0.024073	0.004388	0.021709	86.8	0.505
0.5 $MgCl_2$	1	0.25	4.000		0.021529		0.019505	78.0	0.605
0.7 $CaCl_2$	1	0.35	2.8571	0.053615	0.032700	0.007325	0.028817	82.3	0.558
0.7 $MgCl_2$	1	0.35	2.8571		0.028240		0.024798	70.9	0.549
0.9 $CaCl_2$	1	0.45	2.2222	0.065080	0.039688	0.010791	0.033822	75.2	0.510
0.9 $MgCl_2$	1	0.45	2.2222		0.036183		0.031258	69.5	0.538
1.3 $CaCl_2$	1	0.65	1.538	0.082101	0.054236	0.019999	0.043256	66.9	0.454
1.3 $MgCl_2$	1	0.65	1.538		0.047864		0.038575	59.3	0.460
1.7 $CaCl_2$	1	0.85	1.1765	0.094339	0.066903	0.03017	0.050933	59.9	0.406
1.7 $MgCl_2$	1	0.85	1.1765		0.057606		0.043406	51.1	0.396
2.1 $CaCl_2$	1	1.05	0.9523	0.10078	0.078244	0.04374	0.055264	52.6	0.357
2.1 $MgCl_2$	1	1.05	0.9523		0.066280		0.04552	43.4	0.336
2.5 $CaCl_2$	1	1.25	0.8000	0.10278	0.088853	0.05957	0.057913	46.3	0.314
2.5 $MgCl_2$	1	1.25	0.8000		0.073499		0.044869	35.9	0.278
2.9 $CaCl_2$	1	1.45	0.68966	0.10007	0.097385	0.07536	0.058845	40.6	0.275
2.9 $MgCl_2$	1	1.45	0.68966		0.978040		0.04122	28.4	0.220

Table XXVII.—*Weight-Normal Corrections.*

m.	*P.*	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction per cent.
0.3 $CaCl_2$	1	25.6460	0.77345	24.87255	0.5
0.3 $MgCl_2$	1				
0.5 $CaCl_2$	1	26.0314	1.28915	24.74225	1.0
0.5 $MgCl_2$	1				
0.7 $CaCl_2$	1	26.4594	1.80475	24.65465	1.4
0.7 $MgCl_2$	1				
0.9 $CaCl_2$	1	26.8453	2.32045	24.52485	1.9
0.9 $MgCl_2$	1				
1.3 $CaCl_2$	1	27.6088	3.35175	24.25705	3.0
1.3 $MgCl_2$	1				
1.7 $CaCl_2$	1	28.3821	4.38305	23.99905	4.0
1.7 $MgCl_2$	1				
2.1 $CaCl_2$	1	29.1096	5.41435	23.69525	5.2
2.1 $MgCl_2$	1				
2.5 $CaCl_2$	1	29.8333	6.44555	23.38775	6.5
2.5 $MgCl_2$	1				
2.9 $CaCl_2$	1	30.5280	7.47695	23.05105	8.8
2.9 $MgCl_2$	1				

In Table XXVIII., m_c = normal concentration of each salt in the mixture. α = dissociation of each salt in the mixture, as given in Table XXVI. mL = lowering of freezing point, calculated from formula $[(1.86 \times 2\alpha) + 1.86]m$. The correction percentage is deduced on the assumption that the two salts form the same hydrates in the mixture that they form in separate solutions. Upon this assumption the amount of water which each salt would eliminate from the sphere of action as solvent is calculated from the formula

$$1{,}000 - \left[\frac{L}{\underline{L}} \times 1{,}000\right].$$

The values for magnesium chloride and calcium chloride are added together, and to this is added also the difference between 1000 grams and the amount of water actually present in one liter as given by the weight-normal corrections. This, then, is given as a percentage correction in the column headed "Correction, per cent." The value mL is divided by this percentage, and the result given under Δ.

Table XXVIII.

m.	P.	m_c.	α.	mL.	Correction, per cent.	Δ.
0.3 $CaCl_2$	1	0.15	0.636	0°.634	78.9	0°.803
0.3 $MgCl_2$	1		0.664	0°.650		0°.823
0.5 $CaCl_2$	1	0.25	0.589	1°.012	68.0	1°.488
0.5 $MgCl_2$	1		0.605	1°.027		1°.510
0.7 $CaCl_2$	1	0.35	0.558	1°.378	58.8	2°.345
0.7 $MgCl_2$	1		0.549	1°.366		2°.325
0.9 $CaCl_2$	1	0.45	0.510	1°.690	51.2	3°.298
0.9 $MgCl_2$	1		0.538	1°.738		3°.392
1.3 $CaCl_2$	1	0.65	0.454	2°.360	38.5	5°.998
1.3 $MgCl_2$	1		0.460	2°.321		6°.035
1.7 $CaCl_2$	1	0.85	0.406	2°.865	25.81	1°.13
1.7 $MgCl_2$	1		0.396	2°.832		11°.00
2.1 $CaCl_2$	1	1.05	0.357	3°.346	14.7	22°.85
2.1 $MgCl_2$	1		0.336	3°.264		22°.29

Evidently the sum of the values of Δ for calcium chloride and magnesium chloride, as thus found, should equal the lowering found experimentally for the mixture in question. These values are placed side by side, for comparison, in

Table XXIX.

m.	P.	m_c.	Δ (*calculated*).	Δ (*Exp.*).	Diff.
0.3 $CaCl_2$	1	0.15	1°.626	1.553	0.073
0.3 $MgCl_2$	1	0.15			
0.5 $CaCl_2$	1	0.25	2°.998	2.704	0.294
0.5 $MgCl_2$	1	0.25			
0.7 $CaCl_2$	1	0.35	4°.670	4.053	0.617
0.7 $MgCl_2$	1	0.35			
0.9 $CaCl_2$	1	0.45	6°.690	5.543	1.147
0.9 $MgCl_2$	1	0.45			
1.3 $CaCl_2$	1	0.65	12°.033	9.320	2.713
1.3 $MgCl_2$	1	0.65			
1.7 $CaCl_2$	1	0.85	22°.13	13.5	8.629
1.7 $MgCl_2$	1	0.85			
2.1 $CaCl_2$	1	1.05	45°.14	19.5	25.64
2.1 $MgCl_2$	1	1.05			

It is unnecessary to extend these calculations to the remaining, more concentrated mixtures, since it is evident that the differences between the values calculated on the basis that the two salts form the same hydrates in separate solutions that they form in the mixtures and the values for Δ obtained experimentally become increasingly larger with increase in concentration. It is further evident that the hypothesis is untenable from the fact that it would call for the elimination of 944 grams of water per liter of solution in the case of the 2.5 N mixture of the above salts, and of 1047 grams in the case of the 2.9 N mixture.

At the moment of mixing the two solutions, each salt is prevented from forming the hydrate which it ordinarily forms in separate solution by the amount of water which has been eliminated from the sphere of action as solvent in the formation of the hydrate of the other component of the mixture. Consequently, for the more dilute solutions at least, the hydrates formed by a salt in separate solution should be related to the hydrates formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the single solution is related to the amount present as solvent in the mixture. For example, take calcium chloride and magnesium chloride, 0.15 N solutions of each. Referring to Tables XX. and XXIV., if X represents the unknown value of M for calcium chloride, in the mixture $6 : X :: 1000 : 897$. 6.0 is the value of M for 0.15 N calcium chloride in separate solution, and this has been corrected to 1000 grams of solvent. The figure 897 is found by subtracting from 1000 the number of grams of water with which the magnesium chloride combines, when it forms the hydrate indicated for the concentration in question in Table XXIV., plus the difference between the amount of water present in the solution and 1000 grams, as given by the weight-normal correction.

Having thus obtained the values of M for the salts in the mixture, it is possible to solve for L' from the equation

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18},$$

where L represents the theoretical lowering found for the salt by calculating it from the value of α, which has been determined for the mixture in question. This value of L' must then be corrected, in order to obtain the value as it would be observed, by dividing it by the proper per cent. This percentage correction is found by deducing the number of grams of water eliminated as water of hydration by the other salt in the mixture, basing the calculation upon the value of M worked out for the mixture. To this must be added the percentage correction which the weight-normal correction has given.

The sum of these values for L' for the two salts in the mixture should then be equal to Δ as found experimentally for the mixture, provided this hypothesis is correct. In the following tables the values thus obtained are given.

$M_c =$ the value for M deduced from the proportion.

$L'_c =$ the value for L' calculated upon this value of M.

$L'^{Cor.}_c =$ the value for L', with proper percentage correction.

Sum = the sum of these two values for $L'^{Cor.}_c$, multiplied by the normality of the solution.

$\Delta =$ the lowering found experimentally for the same mixture.

The other symbols employed have the usual significance.

Without further extending this method of calculation, it is evident that it does not give the true value of the hydrates formed, and that the hydrating power is larger for the more concentrated mixtures than would be indicated by the proportions given below.

This is just what we should expect, for with increasing hydration we do not have the process of loss of water from the hydrates formed in separate solution going on to the end in the mixture, but instead, we have, necessarily, a condition of equilibrium between the hydrating powers of the two salts. Also, as a direct result, the amount of water thus left uncombined affects the final composition of the hydrates, as already indicated.

This condition of equilibrium is not represented by the proportions given above, since the amount of water playing the part of solvent is not that indicated by these proportions.

Table XXX.

m.	P.	m_c.	M.	M_c.	L.	L′.	$L'^{C.or}_c$	Sum.	Δ.
0.3 $CaCl_2$	1	0.15	6.0	5.4	4.224	4.682	5.16	1°.57	1.553
0.3 $MgCl_2$	1	0.15	5.5	4.9	4.330	4.748	5.29		
0.5 $CaCl_2$	1	0.25	8.2	6.8	4.109	4.685	5.52	2°.74	2.704
0.5 $MgCl_2$	1	0.25	9.2	7.8	4.050	4.715	5.44		
0.7 $CaCl_2$	1	0.35	9.7	7.5	3.936	4.547	5.71	3°.97	4.053
0.7 $MgCl_2$	1	0.35	12.7	10.5	3.902	4.808	5.64		
0.9 $CaCl_2$	1	0.45	11.7	8.6	3.755	4.438	5.77	5°.26	5.543
0.9 $MgCl_2$	1	0.45	14.9	11.8	3.862	4.897	5.92		
1.3 $CaCl_2$	1	0.65	15.7	10.7	3.548	4.394	5.94	7°.74	9.32
1.3 $MgCl_2$	1	0.65	17.8	12.8	3.570	4.639	5.97		
1.7 $CaCl_2$	1	0.85	18.9	11.5	3.371	4.251	6.06	10°.21	13.5
1.7 $MgCl_2$	1	0.85	21.7	14.3	3.332	4.487	5.96		

If we consider that the values of M for calcium chloride and for magnesium chloride in separate solutions, since their hydrating powers are nearly equal, represent the relative hydrating powers under the same conditions for the two salts, at the concentration corresponding to any pair of values of M, then it becomes possible to calculate the approximate composition of the hydrates of calcium chloride and magnesium chloride in the mixture. Selecting, for example, the mixture consisting of 1 part of 1.7 N calcium chloride and 1 part of 1.7 N magnesium chloride, then:

Let X equal the number of grams of water eliminated in the formation of the hydrate of calcium chloride which occurs in the mixture in question. If the hydrates of calcium chloride and magnesium chloride in the mixture are related as they are in separate solutions, they will be to each other as 18.9: 21.7 (see Tables XX. and XXIV.), hence,

$\frac{217}{189}X$ = the number of grams of water eliminated in the formation of hydrate of magnesium chloride in the mixture.

From the equation

$$M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18},$$

we have

$$X = 1000 - \frac{3371}{L'_{Ca}} \qquad (1),$$

where 3.371 is the lowering found for 0.85 N calcium chloride by calculation from the value of α given in Table XXVI., and L'_{Ca} = the lowering observed for calcium chloride, corrected properly for water less than 1000 grams, and multiplied by m.

Similarly,

$$\frac{217}{189}X = 1000 - \frac{3332}{L'_{Mg}} \qquad (2).$$

Let L'_O = *observed* lowering due to magnesium chloride. Then, $13^\circ.5 - L'_O$ = *observed* lowering due to calcium chloride (*vide* Table XXV.).

Then

$$L'_O = \frac{L'_{Mg} \times 0.85}{1 - \frac{X}{1000} - \frac{4}{100}} \quad (3),$$

where 0.85 is the normality in question, and the denominator is the necessary percentage correction, based upon the value of X and the correction given in Table XXVII.

Similarly,

$$13.5 - L'_O = \frac{L'_{Ca} \times 0.85}{1 - \frac{\frac{217}{189} X}{1000} - \frac{4}{100}} \quad (4).$$

From equation (1),

$$L'_{Ca} = \frac{3371}{1000 - X} \quad (5).$$

From equation (2),

$$L'_{Mg} = \frac{3332}{1.000 - 1.148 X} \quad (6).$$

Eliminating L'_O by combining equations (3) and (4), and then substituting the values of L'_{Ca} and L'_{Mg} from (5) and (6), it becomes possible to solve for X. By this method the values of M for calcium chloride and magnesium chloride in this mixture are found to be 17.1 and 19.6, respectively.

By the above methods the values of M for the mixtures between 0.9 N and 2.9 N have been derived, and are given in the following table, under M_c. The abbreviations at the top of each column have the usual significance, the suffix c indicating that the values are for the salt *in the mixture.*

For the sake of comparison, the values of M for calcium chloride and magnesium chloride in separate solutions are plotted as curves, against concentration (as axis of abscissas). Upon the same sheet are drawn similar curves for the values of M in the mixture.

Table XXXI.

m.	*P.*	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp Gr. Cor.	*Mc.*	*Hc.*
1.3 $CaCl_2$	1	0.65	0.454	3.548	15.74	9.32	3.0	14.5	22.3
1.3 $MgCl_2$	1	0.65	0.460	3.570	17.79			16.4	25.2
1.7 $CaCl_2$	1	0.85	0.406	3.371	18.92	13.5	4.0	17.1	20.1
1.7 $MgCl_2$	1	0.85	0.396	3.332	21.73			19.6	23.1
2.1 $CaCl_2$	1	1.05	0.357	3.187	21.92	19.5	5.2	19.8	18.9
2.1 $MgCl_2$	1	1.05	0.336	3.264	25.06			22.7	21.6
2.5 $CaCl_2$	1	1.25	0.314	3.028	24.32	27.25	6.5	22.8	18.2
2.5 $MgCl_2$	1	1.25	0.278	2.895	28.14			26.3	21.0
2.9 $CaCl_2$	1	1.45	0.275	2.883	27.29	37.0	7.8	25.9	17.9
2.9 $MgCl_2$	1	1.45	0.220	2.479	30.86			28.9	19.9

Upon comparing curve I., the hydration of magnesium chloride alone, with curve IV., the hydration of the calcium chloride in the mixture, it will be seen that where I. rises IV. falls, and *vice versa*. This is exactly what we should expect, since an increase in the hydrating power of magnesium chloride should result in a corresponding decrease in the amount of water with which the calcium chloride would be able to combine in the mixture, unless a corresponding increase in the hydrating power of the calcium chloride in separate solution should also occur. Again, comparing curves I. and II., and III. and IV., the hydrates in separate solution and in the

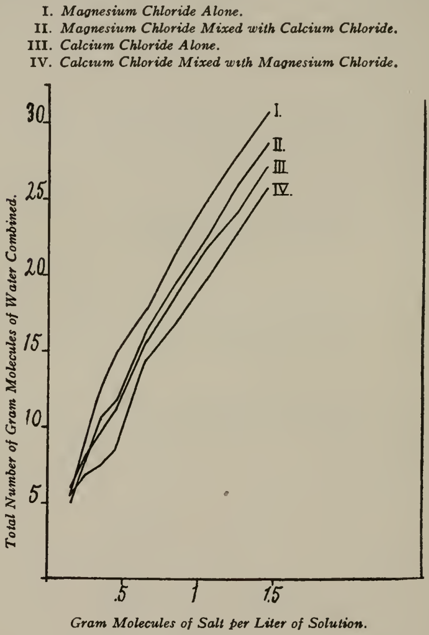


Fig. III.

mixture are of the same general order of magnitude, except where the presence of the one salt in the mixture alters the composition of the hydrate formed by the other.

It was thought desirable to compare the effect of a salt with less hydrating power mixed with one of greater hydrating power.

For this purpose calcium chloride and strontium chloride were selected, the hydrating power of strontium chloride being somewhat less than that of calcium chloride

The data for the separate solutions of calcium chloride have already been given. Those of strontium chloride follow.

STRONTIUM CHLORIDE.

Table XXXII.—Freezing Point Measurements.

m.	Δ.	Δ/m.	m.	Δ.	Δ/m.
0.15	0°.753	5.02	0.65	3°.521	5.42
0.25	1°.249	5.00	0.85	4°.863	5.72
0.35	1°.774	5.07	1.05	6°.354	6.05
0.45	2°.333	5.18	1.23541	7°.861	6.36

Table XXXIII.—Conductivity Measurements.

m.	V.	k.	Λ_v.	α.
0.15	6.6666	0.015377	102.5	0.747
0.25	4.0000	0.024185	96.7	0.705
0.35	2.8571	0.032590	93.1	0.678
0.45	2.2222	0.040479	90.0	0.655
0.65	1.5380	0.055017	84.6	0.616
0.85	1.1764	0.067824	79.8	0.581
1.05	0.9523	0.079796	76.0	0.553
1.23541	0.8945	0.088607	71.7	0.522

Table XXXIV.—Weight-Normal Corrections.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction, per cent.
0.15	25.5325	0.59437	24.94810	0.3
0.25	25.8496	0.99060	24.85898	0.6
0.35	26.1900	1.38688	24.8031	0.8
0.45	26.5388	1.7831	24.7557	1.0
0.65	27.1944	2.5756	24.6188	1.5
0.85	27.8553	3.3681	24.4872	2.1
1.05	28.5672	4.1606	24.4066	2.4
1.23541	29.1297	4.8954	24.2344	3.1

Table XXXV.—Hydrates.

m.	α.	L.	Δ/m.	L′.	M.	H.
0.15	0.747	4.64	5.02	4.99	3.9	26.0
0.25	0.705	4.48	5.00	4.97	5.5	22.0
0.35	0.678	4.39	5.07	5.03	7.1	20.3
0.45	0.655	4.30	5.18	5.13	9.0	20.0
0.65	0.616	4.15	5.42	5.34	12.4	19.1
0.85	0.581	4.02	5.72	5.60	15.7	18.5
1.05	0.553	3.93	6.05	5.91	18.7	17.8
1.23541	0.522	3.80	6.36	6.17	21.3	17.2

MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

Table XXXVI.—Freezing Point Measurements.

m.	P.	Δ.	m.	P.	Δ.
0.3 $CaCl_2$	1	1°.503	1.3 $CaCl_2$	1	8°.682
0.3 $SrCl_2$	1		1.3 $SrCl_2$	1	
0.5 $CaCl_2$	1	2°.626	1.7 $CaCl_2$	1	12°.924
0.5 $SrCl_2$	1		1.7 $SrCl_2$	1	
0.7 $CaCl_2$	1	3°.906	2.1 $CaCl_2$	1	18°.290
0.7 $SrCl_2$	1		2.1 $SrCl_2$	1	
0.9 $CaCl_2$	1	5°.310	2.5 $CaCl_2$	1	Salt separated out.
0.9 $SrCl_2$	1		2.5 $SrCl_2$	1	

Table XXXVII.—Conductivity Measurements.

m.	*P.*	*mc.*	*Vc.*	*ku.*	*k.*	*D.*	*kc.*	Λ_v.	*α.*
0.3 $CaCl_2$	1	0.15	6.6666	0.014991	0.028239	0.002129	0.013837	92.3	0.625
0.3 $SrCl_2$	1	0.15	6.6666	0.015377			0.014402	96.0	0.699
0.5 $CaCl_2$	1	0.25	4.0000	0.024073	0.043980	0.004278	0.021775	87.1	0.590
0.5 $SrCl_2$	1	0.25	4.0000	0.024185			0.022205	83.8	0.647
0.7 $CaCl_2$	1	0.35	2.8571	0.032700	0.051880	0.007102	0.028900	82.6	0.560
0.7 $SrCl_2$	1	0.35	2.8571	0.032590			0.029290	83.7	0.610
0.9 $CaCl_2$	1	0.45	2.2222	0.039688	0.070491	0.009676	0.034456	76.6	0.519
0.9 $SrCl_2$	1	0.45	2.2222	0.040479			0.036035	80.1	0.583
1.3 $CaCl_2$	1	0.65	1.5380	0.054236	0.090731	0.018522	0.044245	68.1	0.461
1.3 $SrCl_2$	1	0.65	1.5380	0.055017			0.046486	71.5	0.521
1.7 $CaCl_2$	1	0.85	1.1765	0.066903	0.105560	0.029177	0.051170	60.2	0.408
1.7 $SrCl_2$	1	0.85	1.1765	0.067824			0.054389	64.0	0.466
2.1 $CaCl_2$	1	1.05	0.9523	0.078244	0.114280	0.043760	0.054584	52.0	0.352
2.1 $SrCl_2$	1	1.05	0.9523	0.079796			0.059696	56.9	0.414

Table XXXVIII.—Weight-Normal Corrections.

m.	*P.*	$W_{sol.}$	$W_{salt.}$	W_{H_2O}	Correction, per cent.
0.3 $CaCl_2$	1	25.8463	1.0106	24.8357	0.7
0.3 $SrCl_2$	1				
0.5 $CaCl_2$	1	26.4106	1.6844	24.7262	1.1
0.5 $SrCl_2$	1				
0.7 $CaCl_2$	1	26.9452	2.3581	24.5871	1.7
0.7 $SrCl_2$	1				
0.9 $CaCl_2$	1	27.4711	3.0319	24.4392	2.2
0.9 $SrCl_2$	1				
1.3 $CaCl_2$	1	28.5671	4.3794	24.1877	3.3
1.3 $SrCl_2$	1				
1.7 $CaCl_2$	1	29.6381	5.7269	23.9112	4.4
1.7 $SrCl_2$	1				
2.1 $CaCl_2$	1	30.6744	7.0744	23.6031	5.6
2.1 $SrCl_2$	1				

For the sake of comparison, the lowerings of the freezing point which would be obtained from the mixture of calcium chloride and strontium chloride are given in Table XXXIX., basing them upon the same method of calculation as that already given in detail for Table XXX. The symbols used have the same significance in the two tables.

It will be noted that in Table XXXIX., again, as in the case of the mixture of calcium chloride and magnesium chloride, the difference between the lowering as calculated upon the hypothesis that, for the more dilute solutions, at least, the hydrates formed by a salt in separate solution are related to the hydrates formed by the same salt in the mixture at corresponding concentrations as the amount of water present as solvent in the mixture—the difference between this and the lowering found experimentally becomes increasingly large. This has already been discussed in the preceding case.

The method of calculating the composition of the hydrates existing in a mixture of two salts with about the same hydrating power, such as calcium chloride and magnesium chloride, was based upon the assumption that the values of M in their separate solutions represent the relative hydrating powers under the same conditions for the two salts in their mixtures. While this applies where the hydrates formed are

Table XXXIX.

m.	*P.*	*mc.*	*M.*	*Mc.*	*L.*	*L'c.*	$L'^{cor.}_{c.}$	Sum.	Δ.
0.3 $CaCl_2$	1	0.15	6.0	5.6	4.186	4.65	5.00	1.548	1.503
0.3 $SrCl_2$	1	0.15	3.9	3.5	4.461	4.76	5.32		
0.5 $CaCl_2$	1	0.25	8.2	7.3	4.056	4.67	5.16	2.646	2.626
0.5 $SrCl_2$	1	0.25	5.5	4.6	4.266	4.65	5.43		
0.7 $CaCl_2$	1	0.35	9.7	8.3	3.942	4.63	5.26	3.771	3.906
0.7 $SrCl_2$	1	0.35	7.1	5.7	4.127	4.60	5.51		
0.9 $CaCl_2$	1	0.45	11.7	9.5	3.791	4.57	5.36	4.979	5.370
0.9 $SrCl_2$	1	0.45	9.0	6.9	4.030	4.60	5.70		
1.3 $CaCl_2$	1	0.65	15.7	11.7	3.576	4.53	5.56	7.465	8.682
1.3 $SrCl_2$	1	0.65	12.4	8.5	3.797	4.48	5.92		
1.7 $CaCl_2$	1	0.85	18.9	12.8	3.378	4.39	5.61	9.877	12.924
1.7 $SrCl_2$	1	0.85	15.7	9.7	3.593	4.35	6.00		
2.1 $CaCl_2$	1	1.05	21.9	13.3	3.171	4.17	5.49	11.99	18.290
2.1 $SrCl_2$	1	1.05	18.7	10.3	3.40	4.17	5.92		

of approximately the same degree of complexity, it would involve an error in the case of two salts of very different hydrating powers. For, if the power of forming hydrates, *i. e.*, of eliminating water from the sphere of action as solvent, differs, then, when two such substances are mixed, if a decrease in the amount of water eliminated from the sphere of action as solvent occurs, this decrease must be assigned to the two salts inversely as their values of M in separate solutions. This follows from a consideration of the fact that the salt with greater hydrating power will have, consequently, greater power of dehydrating the salt with lesser hydrating power. Therefore, the salt which has less power to unite with water must suffer the greater loss in water of hydration in the presence of the salt with stronger hydrating power.

Upon this assumption the following method of calculating the approximate composition of the hydrates in such a mixture has been worked out. Take the case of a mixture consisting of one volume of 0.3 N strontium chloride and one volume of 0.3 N calcium chloride:

Let X equal the total decrease in the number of grams of water eliminated from the sphere of action as solvent in the mixture, as compared with that eliminated in the separate solutions.

Then $\frac{39}{99}X =$ the diminution in the number of grams of water eliminated by the calcium chloride, and $\frac{60}{99}X =$ the diminution in the number of grams of water eliminated by the strontium chloride (see Tables XX. and XXXV. for the values of M in separate solutions).

108.5 grams of water were eliminated by the calcium chloride as water of hydration in the 0.15 N separate solution of that salt (see Table XX.). 70.5 grams were eliminated by the strontium chloride (see Table XXXV.). Therefore,

$$108.5 - 0.39X = 1000 - \frac{4186}{L'_{Ca}} \qquad (1),$$

and

$$70.5 - 0.61\,X = 1000 - \frac{4461}{L'_{Sr}} \qquad (2).$$

$$L'_{Ca} = \frac{4186}{891.5 + 0.39\,X}, \text{ and } L'_{Sr} = \frac{4461}{929.5 + 0.61\,X}.$$

Let L'_O = observed lowering for calcium chloride in the mixture, then,

$$L'_O = \frac{4186 \times 0.15}{891.5 + 0.39\,X} \div \frac{922.5 + 0.61\,X}{1000} \qquad (3), \text{ and}$$

$$1.503 - L'_O = \frac{4461 \times 0.15}{929.5 + 0.61\,X} \div \frac{884.5 + 0.39\,X}{1000} \qquad (4).$$

Combining equations (3) and (4),

$$1.503 = \frac{4186 \times 0.15}{822 + 0.904\,X + .0002379\,X^2} + \frac{4461 \times 0.15}{822 + 0.902\,X + 0.0002379\,X^2}.$$

From this equation the approximate value of X can be obtained. The values of M and H for the mixture of calcium chloride and strontium chloride, thus obtained, are given in Table XL. The symbols have the usual significance.

For the sake of comparison, the values of M for the separate solutions of calcium chloride and strontium chloride and those for the mixture of the two salts have been plotted as curves in Fig. IV.

We find that the results expressed in Fig. IV. are of the same character as those shown in Fig. III. for the mixture of calcium chloride and magnesium chloride. The curve of hydration of each salt in the mixture is parallel to the curve of its hydration in the single solution, except where large values, as shown in curve I., for calcium chloride alone have produced a corresponding lessening in the amount of water with which the strontium chloride has been able to unite in the mixture at a normality of 0.15 to 0.35. An increase in the hydrating power of the calcium chloride must necessarily be accompanied by a corresponding decrease in the complexity of the hydrates of strontium chloride.

In order to compare the difference in the amount of water present as solvent in the single solution and in the mixture with the difference in the value of M in the two cases, these

Table XL.

m.	P.	m_c.	α.	L_c.	M.	Δ.	Sp. Gr. Cor.	M_c.	H_c.
0.3 $CaCl_2$	1	0.15	0.625	4.186	6.0	1.503	0.7	5.1	34.0
0.3 $SrCl_2$	1	0.15	0.699	4.461	3.9			2.4	16.0
0.5 $CaCl_2$	1	0.25	0.590	4.056	8.2	2.626	1.1	7.3	29.2
0.5 $SrCl_2$	1	0.25	0.647	4.266	5.5			4.2	16.8
0.7 $CaCl_2$	1	0.35	0.560	3.942	9.7	3.906	1.6	9.3	26.1
0.7 $SrCl_2$	1	0.35	0.610	4.127	7.1			6.5	18.6
0.9 $CaCl_2$	1	0.45	0.519	3.791	11.7	5.310	2.2	11.1	24.7
0.9 $SrCl_2$	1	0.45	0.583	4.03	9.0			8.3	18.2
1.3 $CaCl_2$	1	0.65	0.461	3.576	15.7	8.682	3.3	15.1	23.2
1.3 $SrCl_2$	1	0.65	0.521	3.797	12.4			11.6	17.8
1.7 $CaCl_2$	1	0.85	0.408	3.378	18.9	12.924	4.4	18.3	21.5
1.7 $SrCl_2$	1	0.85	0.466	3.593	15.7			15.0	17.6
2.1 $CaCl_2$	1	1.05	0.352	3.171	21.9	18.29	5.6	21.5	20.5
2.1 $SrCl_2$	1	1.05	0.414	3.40	18.7			18.2	17.3

values are tabulated. D_{H_2O} is the difference in the amount of water present as solvent in the separate solution and in the mixture. It is found for a given salt by adding to the number of grams of water eliminated as water of hydration by the other salts in the mixture the difference between the correction to weight-normal standard in the case of the separate solution of the salt in question and in the mixture. D_m is the difference between the value of M in the single solution and in the mixture.

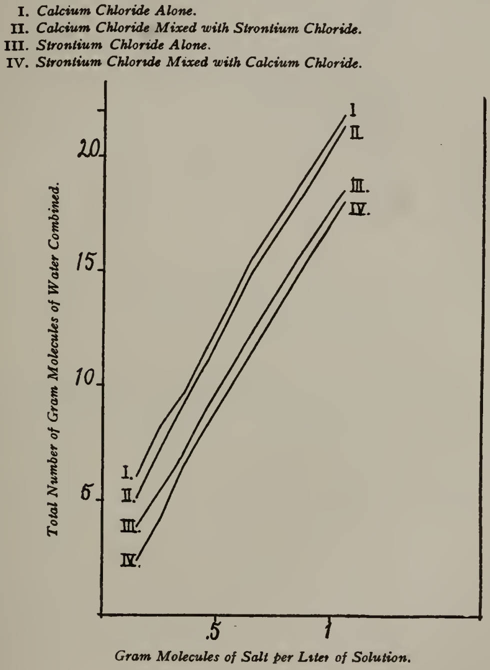


Fig. IV.

Table XLI.—Calcium Chloride in the Mixture of Calcium Chloride and Strontium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	46	0.9	0.65	226	0.6
0.25	81	0.9	0.85	295	0.6
0.35	127	0.4	1.05	359	0.4
0.45	162	0.6			

Table XLII.—Strontium Chloride in the Mixture of Calcium Chloride and Strontium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	96	1.5	0.65	289	0.8
0.25	137	1.3	0.85	353	0.7
0.35	176	0.6	1.05	419	5.0
0.45	212	0.7			

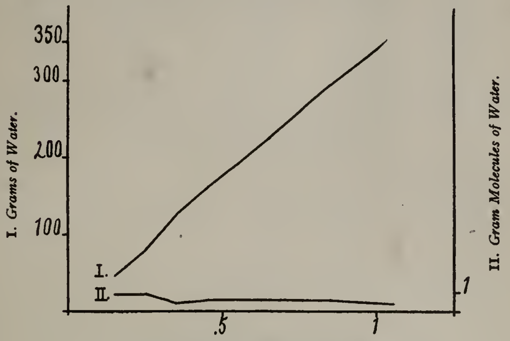
These values are plotted as curves in Figs. V. and VI. The concentrations are the abscissas, and for curve I. the grams of water are taken as ordinates. In curve II. gram molecules of water form the ordinates.

It is readily seen from a comparison of the curves that the decrease in the amount of water present as solvent in the mixture is not accompanied by a corresponding decrease in the values of M. Here again, as in the case of the mixture of calcium chloride and potassium chloride, the difference in the values of M is nearly constant, because the concentration of both salts present in the mixture is increased at the same rate. Slight changes might be manifest if the ions and molecules have different hydrating powers, as seems very probable. Then a decrease in the number of ions and a correspondingly large increase in the number of molecules of dissolved substance present, such as necessarily occurs owing to suppression of the ionization in the mixture, would be accompanied by a change in the number of grams of water combined. That this plays a part in the change noted seems very probable.

For purposes of comparison these same values are given for a few concentrations in the case of calcium chloride and magnesium chloride. The phenomena are of the same kind.

I. *Difference between Water Present as Solvent in Single Solution of Calcium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.*

II. *Difference between the Values of M for Calcium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.*

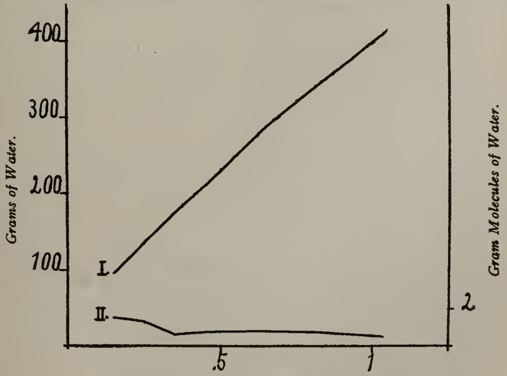


Gram Molecules of Salt per Liter of Solution.

Fig. V.

I. *Difference between Water Present as Solvent in Single Solution of Strontium Chloride and in Mixture of Calcium Chloride and Strontium Chloride.*

II. *Difference between the Values of M for Strontium Chloride in Single Solution and in the Mixture of Calcium Chloride and Strontium Chloride.*



Gram Molecules of Salt per Liter of Solution.

Fig. VI.

Table XLIII.—Calcium Chloride in Calcium Chloride and Magnesium Chloride Mixture.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.65	310.2	1.2	1.25	507.0	1.5
0.85	373.8	1.8	1.45	562.2	1.4
1.05	435.0	2.1			

Table XLIV.—Magnesium Chloride in Calcium Chloride and Magnesium Chloride Mixture.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.65	279	1.4	1.25	450	1.8
0.85	333	2.1	1.45	512	2.0
1.05	389	2.4			

A pair of nitrates was next studied.

The salts must be of such a nature as not to unite to form complexes when mixed, and must have hydrating power. Magnesium nitrate and strontium nitrate were selected. The data for these two salts follow:

MAGNESIUM NITRATE.

Table XLV.—Freezing Point Measurements.

m.	Δ.	Δ/m.	M.	Δ.	Δ/m.
0.15	0°.749	4.99	0.55	3°.019	5.49
0.25	1°.252	5.01	0.65	3°.669	5.64
0.35	1°.805	5.16	0.75	4°.393	5.86
0.45	2°.395	5.32			

Table XLVI.—Conductivity Measurements.

Λ_∞ 0° = 128.5.

m.	V.	k.	Λv.	α.
0.15	6.6666	0.013701	91.3	0.711
0.25	4.0000	0.021563	86.3	0.671
0.35	2.8571	0.028613	81.8	0.636
0.45	2.2222	0.035123	78.1	0.607
0.55	1.8182	0.041506	75.5	0.587
0.65	1.5380	0.046942	72.2	0.562
0.75	1.3333	0.052260	69.7	0.542

Table XLVII.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction, per cent.
0.15	25.4306	0.5567	24.8738	0.5
0.25	25.6880	0.9277	24.7603	1.0
0.35	25.9782	1.2989	24.6794	1.3
0.45	26.2075	1.6610	24.5376	1.8
0.55	26.4748	2.0411	24.4338	2.3
0.65	26.7605	2.4122	24.3484	2.6
0.75	27.0203	2.7833	24.2371	3.1

Table XLVIII.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.15	0.711	4.50	4.99	4.97	5.3	35.1
0.25	0.671	4.36	5.01	4.96	6.7	26.9
0.35	0.636	4.23	5.16	5.09	9.4	26.8
0.45	0.607	4.12	5.32	5.22	11.7	26.0
0.55	0.587	4.05	5.49	5.36	13.6	24.7
0.65	0.562	3.95	5.68	5.49	15.6	24.0
0.75	0.542	3.88	5.86	5.68	17.6	23.5

STRONTIUM NITRATE.

Table XLIX.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.15	0°.674	4.49	0.55	2°.286	4.16
0.25	1°.085	4.34	0.65	2°.681	4.12
0.35	1°.516	4.33	0.75	3°.060	4.08
0.45	1°.903	4.23			

Table L.—Conductivity Measurements.

Λ_∞ 0° = 134.4.

m.	*V.*	*k.*	Λ_v.	*α.*
0.15	6.6666	0.013164	87.8	0.653
0.25	4.0000	0.019905	79.6	0.592
0.35	2.8571	0.025748	73.6	0.548
0.45	2.2222	0.030645	68.1	0.507
0.55	1.8182	0.035106	63.8	0.475
0.65	1.5380	0.038936	59.9	0.446
0.75	1.3333	0.042076	56.1	0.417

Table LI.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction, per cent.
0.15	25.6245	0.7938	24.8307	0.7
0.25	26.0440	1.3542	24.6898	1.2
0.35	26.4408	1.8960	24.5449	1.8
0.45	26.8623	2.4376	24.4247	2.3

Table LI—(Continued).

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.55	27.2890	2.9793	24.3097	2.8
0.65	27.0907	3.5210	24.1697	3.3
0.75	28.0818	4.0627	24.0191	3.9

Table LII.—Hydrates.

m.	α.	*L.*	Δ/m.	*L'.*	*M.*	*H.*
0.15	0.653	4.29	4.49	4.46	2.1	14.1
0.25	0.592	4.06	4.34	4.29	2.98	11.9
0.35	0.548	3.80	4.33	4.25	4.6	13.2
0.45	0.507	3.75	4.23	4.13	5.1	11.4
0.55	0.475	3.63	4.16	4.04	5.6	10.3
0.65	0.446	3.52	4.12	3.98	6.4	9.9
0.75	0.417	3.41	4.08	3.92	7.2	9.6

The data for the *mixture* of magnesium nitrate and strontium nitrate follow:

Table LIII.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.3 $Mg(NO_3)_2$	1	1°.394	1.1 $Mg(NO_3)_2$	1	5°.646
0.3 $Sr(NO_3)_2$	1		1.1 $Sr(NO_3)_2$	1	
0.5 $Mg(NO_3)_2$	1	2.°351	1.3 $Mg(NO_3)_2$	1	6°.893
0.5 $Sr(NO_3)_2$	1		1.3 $Sr(NO_3)_2$	1	
0.7 $Mg(NO_3)_2$	1	3°.371	1.5 $Mg(NO_3)_2$	1	8°.169
0.7 $Sr(NO_3)_2$	1		1.5 $Sr(NO_3)_2$	1	
0.9 $Mg(NO_3)_2$	1	4°.573			
0.9 $Sr(NO_3)_2$	1				

Table LIV.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.3 $Mg(NO_3)_2$	1	26.044	1.3505	24.6936	1.2
0.3 $Sr(NO_3)_2$	1				
0.5 $Mg(NO_3)_2$	1	26.7087	2.2819	24.4268	2.3
0.5 $Sr(NO_3)_2$	1				
0.7 $Mg(NO_3)_2$	1	27.3970	3.1948	24.2022	3.2
0.7 $Sr(NO_3)_2$	1				
0.9 $Mg(NO_3)_2$	1	28.0570	4.1076	23.9435	4.2
0.9 $Sr(NO_3)_2$	1				
1.1 $Mg(NO_3)_2$	1	28.6884	5.0208	23.6681	5.3
1.1 $Sr(NO_3)_2$	1				
1.3 $Mg(NO_3)_2$	1	29.3508	5.9332	23.4177	6.3
1.3 $Sr(NO_3)_2$	1				
1.5 $Mg(NO_3)_2$	1	29.9912	6.8460	23.1452	7.4
1.5 $Sr(NO_3)_2$	1				

Table LV.—Conductivity Measurements

m.	P.	m_c.	V_c.	k_u.	k.	D.	k_c.	Λ_v.	α.
0.3 $Mg(NO_3)_2$	1	0.15	6.6666	0.023842	0.013701	0.003023	0.012288	81.9	0.638
0.3 $Sr(NO_3)_2$	1	0.15	6.6666		0.013164		0.011555	77.0	0.573
0.5 $Mg(NO_3)_2$	1	0.25	4.0000	0.035522	0.021563	0.005946	0.018843	75.4	0.587
0.5 $Sr(NO_3)_2$	1	0.25	4.0000		0.019905		0.016681	66.7	0.497
0.7 $Mg(NO_3)_2$	1	0.35	2.8571	0.044660	0.028613	0.009701	0.024231	69.2	0.539
0.7 $Sr(NO_3)_2$	1	0.35	2.8571		0.025748		0.020429	58.4	0.434
0.9 $Mg(NO_3)_2$	1	0.45	2.2222	0.051704	0.035123	0.014064	0.028881	64.2	0.500
0.9 $Sr(NO_3)_2$	1	0.45	2.2222		0.030645		0.022829	50.7	0.378
1.1 $Mg(NO_3)_2$	1	0.55	1.8182	0.057068	0.041506	0.019526	0.032987	60.0	0.467
1.1 $Sr(NO_3)_2$	1	0.55	1.8182		0.035106		0.024096	43.8	0.326
1.3 $Mg(NO_3)_2$	1	0.65	1.538	0.060997	0.046942	0.024881	0.036202	55.7	0.433
1.3 $Sr(NO_3)_2$	1	0.65	1.538		0.038936		0.024786	38.1	0.284
1.5 $Mg(NO_3)_2$	1	0.75	1.3333	0.063788	0.052260	0.030548	0.039310	52.4	0.408
1.5 $Sr(NO_3)_2$	1	0.75	1.3333		0.042076		0.024476	32.6	0.243

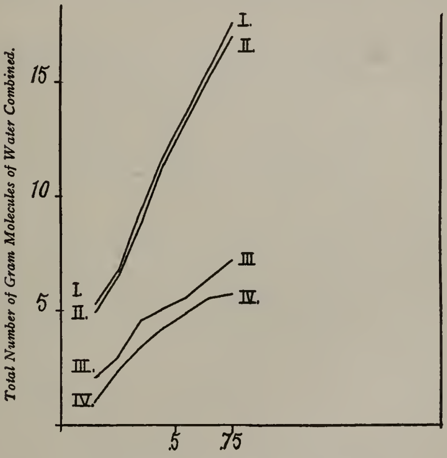
Table LVI.—Hydrates.

m.	*F.*	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
0.3 $Mg(NO_3)_2$	1	0.15	0.638	4.231	5.3	1.394	1.2	4.9	32.5
0.3 $Sr(NO_3)_2$	1	0.15	0.573	3.992	2.1			1.0	6.6
0.5 $Mg(NO_3)_2$	1	0.25	0.587	4.042	6.7	2.351	2.3	6.5	26.0
0.5 $Sr(NO_3)_2$	1	0.25	0.497	3.707	3.0			2.4	9.6
0.7 $Mg(NO_3)_2$	1	0.35	0.539	3.864	9.4	3.371	3.2	8.8	25.1
0.7 $Sr(NO_3)_2$	1	0.35	0.434	3.476	4.6			3.4	9.6
0.9 $Mg(NO_3)_2$	1	0.45	0.500	3.718	11.7	4.513	4.2	11.4	25.3
0.9 $Sr(NO_3)_2$	1	0.45	0.378	3.264	5.1			4.4	9.8
1.1 $Mg(NO_3)_2$	1	0.55	0.467	3.596	13.6	5.646	5.3	13.3	24.2
1.1 $Sr(NO_3)_2$	1	0.55	0.326	3.073	5.6			4.9	8.8
1.3 $Mg(NO_3)_2$	1	0.65	0.433	3.472	15.6	6.892	6.3	15.2	23.4
1.3 $Sr(NO_3)_2$	1	0.65	0.284	2.915	6.4			5.5	8.5
1.5 $Mg(NO_3)_2$	1	0.75	0.408	3.377	17.6	8.169	7.4	17.0	22.7
1.5 $Sr(NO_3)_2$	1	0.75	0.243	2.763	7.2			5.7	7.6

The values of *M* for this mixture are calculated by the method already given. Evidently the same method of calculation applies here as in the case of a mixture of calcium chloride and strontium chloride.

The values of *M*, in single solution and in the mixture, for magnesium nitrate and strontium nitrate have been plotted as curves in Fig. VII. The phenomena are, in general, the same as those already pointed out in preceding cases. Curve IV. deviates from curve III. with increasing concentration, showing the effect of the large increase in the value of *M* for magnesium nitrate, with increasing concentration, upon the amount of water eliminated as water of hydration by the strontium nitrate. The strontium nitrate is dehydrated, partially, by the magnesium nitrate.

I. *Magnesium Nitrate Alone.*
II. *Magnesium Nitrate Mixed with Strontium Nitrate.*
III. *Strontium Nitrate Alone.*
IV. *Strontium Nitrate Mixed with Magnesium Nitrate.*



Gram Molecules of Salt per Liter of Solution.
Fig. VII.

In Tables LVII. and LVIII., we have the differences in the amount of solvent present and in the values of *M*, as previously described for the corresponding tables.

Table LVII.—Magnesium Nitrate in Mixture of Magnesium Nitrate and Strontium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	25	0.4	0.55	118	0.3
0.25	56	0.2	0.65	136	0.4
0.35	80	0.6	0.75	146	0.6
0.45	103	0.3			

Table LVIII.—Strontium Nitrate in Mixture of Magnesium Nitrate and Strontium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.15	93	1.1	0.55	264	0.7
0.25	128	0.6	0.65	304	0.9
0.35	172	1.3	0.75	341	1.5
0.45	224	0.7			

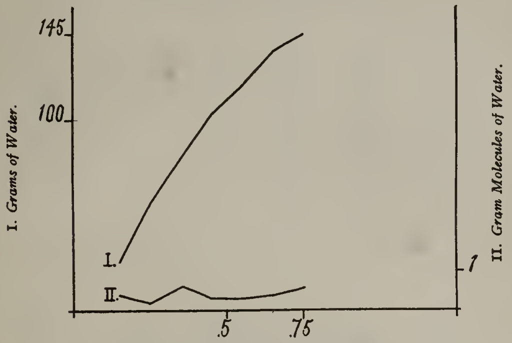
In Figs. VIII. and IX. these values are plotted as curves.

We have here, again, a uniform decrease in the amount of water present as solvent, showing a uniform increase in the hydration with increase in concentration. The curves showing the differences in the values of *M* correspond to a constant difference in the amount of water eliminated in single solution and in the mixture. This constant difference is, of course, due to the fact that the concentration of both salts in the mixture is increased uniformly. The curves show, also, that this difference is slightly affected by the difference in the amount of water present as solvent, since they show a tendency to increase as the diminution in water present as solvent becomes greater.

We next took up a pair of binary electrolytes, LITHIUM BROMIDE *and* SODIUM BROMIDE, *neither of which has a very large hydrating power, the hydrating power of the sodium bromide being somewhat less than that of the lithium bromide.*

I. *Difference between Water Present as Solvent in the Single Solution of Magnesium Nitrate and in Mixture of Magnesium Nitrate and Strontium Nitrate.*

II. *Difference between Values of M for Magnesium Nitrate in Single Solution and in the Mixture of Magnesium Nitrate and Strontium Nitrate.*

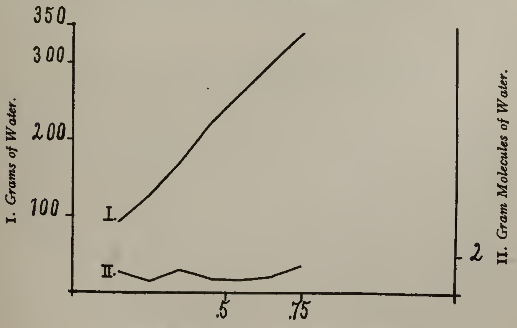


Gram Molecules of Salt per Liter of Solution.

Fig. VIII.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Strontium Nitrate and in the Mixture of Magnesium Nitrate and Strontium Nitrate.*

II. *Difference between the Values of M for Strontium Nitrate in Single Solution and in the Mixture of Magnesium Nitrate and Strontium Nitrate.*



Gram Molecules of Salt per Liter of Solution.

Fig. IX.

SODIUM BROMIDE.

Table LIX.—Freezing Point Measurements.

m.	Δ.	Δ/m.	m.	Δ.	Δ/m.
0.25	0°.895	3.58	0.75	2°.691	3.59
0.35	1°.249	3.57	0.85	3°.054	3.59
0.45	1°.601	3.56	0.95	3°.435	3.62
0.55	1°.946	3.54	1.05	3°.839	3.66
0.65	2°.298	3.54			

Table LX.—Conductivity Measurements.

Λ_∞ 0° = 67.7.

m.	V.	k.	Λ_v.	α.
0.25	4.0000	0.014308	57.2	0.845
0.35	2.8571	0.019628	56.1	0.828
0.45	2.2222	0.024843	55.2	0.815
0.55	1.8182	0.029744	54.1	0.799
0.65	1.5380	0.034269	52.7	0.779
0.75	1.3333	0.039324	52.4	0.774
0.85	1.1765	0.044009	51.8	0.765
0.95	1.0526	0.048853	51.4	0.760
1.05	0.9523	0.053228	50.7	0.747

Table LXI.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.4629	0.6438	24.8191	0.4
0.35	25.7300	0.9014	24.7987	0.8
0.45	25.8823	1.1589	24.7234	1.1
0.55	26.0735	1.4164	24.6571	1.4
0.65	26.2560	1.6727	24.5833	1.7
0.75	26.4535	1.9344	24.5221	1.9
0.85	26.6155	2.1890	24.4265	2.3
0.95	26.8260	2.4465	24.3795	2.5
1.05	27.0072	2.7040	24.3032	2.8

Table LXII.—Hydrates.

m.	*α*.	*L*.	Δ/*m*.	*L′*.	*M*.	*H*.
0.25	0.845	3.43	3.58	3.55	1.9	7.6
0.35	0.828	3.40	3.57	3.54	2.2	6.3
0.45	0.815	3.38	3.56	3.52	2.2	4.9
0.55	0.799	3.35	3.54	3.49	2.2	4.0
0.65	0.779	3.31	3.54	3.48	2.7	4.2
0.75	0.774	3.30	3.59	3.52	3.5	4.6
0.85	0.765	3.28	3.59	3.51	3.6	4.2
0.95	0.760	3.27	3.62	3.53	4.1	4.3
1.05	0.747	3.25	3.66	3.56	4.8	4.6

LITHIUM BROMIDE.

Table LXIII.—Freezing Point Measurements.

m.	Δ.	Δ/*m*.	*m*.	Δ.	Δ/*m*.
0.25	0°.917	3.67	0.75	2°.957	3.94
0.35	1°.292	3.69	0.85	3°.418	4.02
0.45	1°.679	3.75	0.95	3°.900	4.11
0.55	2°.090	3.80	1.05	4°.381	4.17
0.65	2°.514	3.87			

Table LXIV.—Conductivity Measurements.

m.	*V*.	*k*.	Λ*v*.	*α*.
0.25	4.0000	0.012699	50.8	0.848
0.35	2.8571	0.017288	49.4	0.825
0.45	2.2222	0.021694	48.2	0.805
0.55	1.8182	0.025855	47.0	0.785
0.65	1.5380	0.029863	45.9	0.757
0.75	1.3333	0.033996	45.3	0.745
0.85	1.1765	0.057904	44.6	0.734
0.95	1.0526	0.041760	44.0	0.723
1.05	0.9523	0.045505	43.3	0.767

Table LXV.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.3913	0.5437	24.8476	0.6
0.35	25.5641	0.7612	24.8029	0.8
0.45	25.7225	0.9786	24.7439	1.0
0.55	25.8690	1.1961	24.6729	1.3
0.65	26.0358	1.4136	24.6222	1.5
0.75	26.1585	1.6311	24.5274	1.9
0.85	26.3303	1.8485	24.4818	2.1
0.95	26.4558	2.0660	24.3898	2.4
1.05	26.6235	2.2835	24.3400	2.6

Table LXVI.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.25	0.848	3.44	3.67	3.65	3.2	12.8
0.35	0.825	3.39	3.69	3.63	3.7	10.6
0.45	0.805	3.36	3.75	3.71	5.2	11.6
0.55	0.785	3.32	3.80	3.75	6.4	11.6
0.65	0.767	3.29	3.87	3.81	7.5	11.5
0.75	0.757	3.27	3.94	3.87	8.6	11.5
0.85	0.745	3.25	4.02	3.94	9.7	11.4
0.95	0.734	3.23	4.11	4.01	10.8	11.4
1.05	0.723	3.21	4.17	4.06	11.6	11.0

MIXTURE OF LITHIUM BROMIDE AND SODIUM BROMIDE.

Table LXVII.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.5 LiBr	1	1°.823	1.5 LiBr	1	6°.293
0.5 NaBr	1		1.5 NaBr	1	
0.7 LiBr	1	2°.596	1.7 LiBr	1	7°.328
0.7 NaBr	1		1.7 NaBr	1	
0.9 LiBr	1	3°.415	1.9 LiBr	1	8°.399
0.9 NaBr	1		1.9 NaBr	1	
1.1 LiBr	1	4°.325	2.1 LiBr	1	9°.539
1.1 NaBr	1		2.1 NaBr	1	
1.3 LiBr	1	5°.284			
1.3 NaBr	1				

Table LXVIII.—Conductivity Measurements.

m.	P.	m_c.	V_c.	k_u.	k.	D.	k_c.	Λ_v.	α.
0.5 LiBr	1	0.25	4.0000	0.025489	0.012699	0.001518	0.011986	47.9	0.800
0.5 NaBr	1	0.25	4.0000		0.014308		0.013503	54.0	0.798
0.7 LiBr	1	0.35	2.8571	0.034327	0.017288	0.002589	0.016073	45.9	0.767
0.7 NaBr	1	0.35	2.8571		0.019628		0.018254	52.2	0.770
0.9 LiBr	1	0.45	2.2222	0.042727	0.021694	0.003810	0.019905	44.2	0.738
0.9 NaBr	1	0.45	2.2222		0.024843		0.022822	50.7	0.749
1.1 LiBr	1	0.55	1.8182	0.051105	0.025855	0.004494	0.023745	43.2	0.721
1.1 NaBr	1	0.55	1.8182		0.029744		0.027360	49.8	0.735
1.3 LiBr	1	0.65	1.538	0.058945	0.029863	0.005187	0.027248	42.2	0.704
1.3 NaBr	1	0.65	1.538		0.034269		0.031517	48.5	0.716
1.5 LiBr	1	0.75	1.3333	0.066486	0.037904	0.006834	0.030788	41.1	0.685
1.5 NaBr	1	0.75	1.3333		0.044009		0.035698	47.6	0.703
1.7 LiBr	1	0.85	1.1765	0.073132	0.04176	0.008781	0.033841	39.8	0.665
1.7 NaBr	1	0.85	1.1765		0.048853		0.039291	46.2	0.683
1.9 LiBr	1	0.95	1.0526	0.080414	0.045505	0.010199	0.03688	38.8	0.648
1.9 NaBr	1	0.95	1.0526		0.053228		0.043531	45.8	0.677
2.1 LiBr	1	1.05	0.9523	0.086647	0.033996	0.012086	0.039832	37.9	0.633
2.1 NaBr	1	1.05	0.9523		0.039324		0.046815	44.6	0.659

Since lithium bromide and sodium bromide are each binary and dissociated to almost exactly the same extent at equal concentrations of the solutions, the loss in conductivity is apportioned to an equal driving back in the dissociation of the lithium bromide and sodium bromide, except in the mixtures $\left.\begin{array}{l}1.7\ \text{LiBr}\\ 1.7\ \text{NaBr}\end{array}\right\}$ and $\left.\begin{array}{l}1.9\ \text{LiBr}\\ 1.9\ \text{NaBr}\end{array}\right\}$, where the slight difference in the dissociation of the separate solutions is taken into account.

Table LXIX.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.5 LiBr	1	25.9003	1.18748	24.7128	1.1
0.5 NaBr	1				
0.7 LiBr	1	26.2462	1.6625	24.5837	1.7
0.7 NaBr	1				
0.9 LiBr	1	26.6053	2.1375	24.4678	2.1
0.9 NaBr	1				
1.1 LiBr	1	26.9317	2.6125	24.3192	2.7
1.1 NaBr	1				
1.3 LiBr	1	27.2984	3.0863	24.2121	3.2
1.3 NaBr	1				
1.5 LiBr	1	27.5978	3.5625	24.0353	3.9
1.5 NaBr	1				
1.7 LiBr	1	27.9400	4.0375	23.9025	4.4
1.7 NaBr	1				
1.9 LiBr	1	28.2890	4.5125	23.7765	4.9
1.9 NaBr	1				
2.1 LiBr	1	28.6065	4.9875	23.6190	5.5
2.1 NaBr	1				

Table LXX.—Hydrates.

m.	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
0.5 LiBr	0.25	0.800	3.349	3.2	1.823	1.1	2.8	11.2
0.5 NaBr	0.25	0.798	3.344	1.9			1.2	4.8
0.7 LiBr	0.35	0.767	3.286	3.7	2.596	1.7	3.5	10.0
0.7 NaBr	0.35	0.770	3.293	2.2			2.0	5.7
0.9 LiBr	0.45	0.738	3.233	5.2	3.415	2.1	5.2	11.5
0.9 NaBr	0.45	0.749	3.253	2.2			2.0	4.5
1.1 LiBr	0.55	0.721	3.201	6.4	4.325	2.7	6.7	12.2
1.1 NaBr	0.55	0.735	3.227	2.2			2.3	4.2
1.3 LiBr	0.65	0.704	3.107	7.5	5.284	3.2	8.0	12.3
1.3 NaBr	0.65	0.716	3.192	2.7			2.9	4.5
1.5 LiBr	0.75	0.685	3.135	8.6	6.293	3.9	8.9	11.8
1.5 NaBr	0.75	0.703	3.168	3.5			3.6	4.8

P = 1 in every case.

Table LXX.—(Continued).

m.	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
1.7 LiBr	0.85	0.665	3.096	9.7	7.328	4.4	10.2	12.0
1.7 NaBr	0.85	0.683	3.130	3.6			3.8	4.4
1.9 LiBr	0.95	0.648	3.065	10.8	8.399	4.9	11.0	11.6
1.9 NaBr	0.95	0.677	3.119	4.1			4.2	4.4
2.1 LiBr	1.05	0.633	3.038	11.6	9.539	5.5	11.6	11.0
2.1 NaBr	1.05	0.659	3.085	4.8			4.8	4.6

P — equals 1 in every case.

The values of *M* and *H* for this mixture are calculated upon the same basis as that previously employed in the mixture of magnesium nitrate and strontium nitrate. The values thus obtained for the mixture of lithium bromide and sodium bromide are given in the following table:

Curve II., Fig. X., representing the value of *M* in the mixture of lithium bromide and sodium bromide, crosses curve I., the value of *M* for lithium bromide in single solution. The same phenomena presents itself in the case

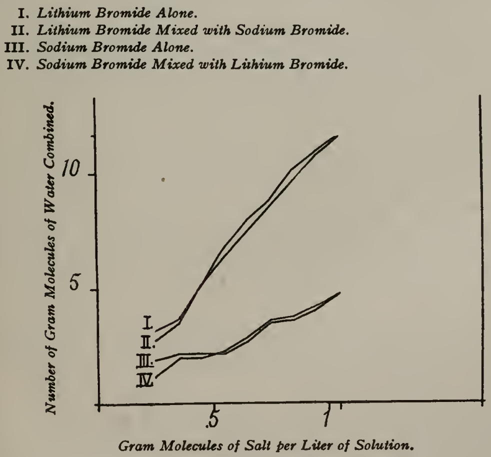


Fig. X.

of sodium bromide at a somewhat greater concentration. In an earlier part of this paper it was suggested that the hydrating power of the ions alone and of these ions when combined to form molecules would probably be different. If, now, the hydrating power of the lithium bromide and the sodium bromide molecules is greater than that of the respective ions, we might expect that the effect of the smaller amount of water present as solvent in the mixture would be overcome by the greater hydrating power of the undissociated molecules. Evidently, for this increased hydrating power of the molecules over the ions to show itself in the resulting curve, the other salt in the mixture must have little hydrating power and a comparatively small molecular weight, for if the molecular weight is large, so much solvent will be displaced when the solutions are made up volume normal that the decreased amount of solvent will obscure any change in hydration due to other causes. Also, the difference in the hydrating power of the ions and molecules should be considerable, in order to overcome the effect of decrease in amount of solvent present with increase in concentration.

The difference between the amount of water acting as solvent towards each salt in the mixture and in single solution, and the differences between the values of M in the same cases, are given in the following tables. A negative value of D_m indicates that the number of grams of water eliminated by a salt in a mixture is greater, instead of less, than in single solution.

Table LXXI.—Lithium Bromide in Mixture of Lithium Bromide and Sodium Bromide.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	27	0.4	0.75	85	—0.3
0.35	45	0.2	0.85	91	—0.3
0.45	47	0.0	0.95	101	—0.2
0.55	55	—0.3	1.05	115	0.0
0.65	69	—0.5			

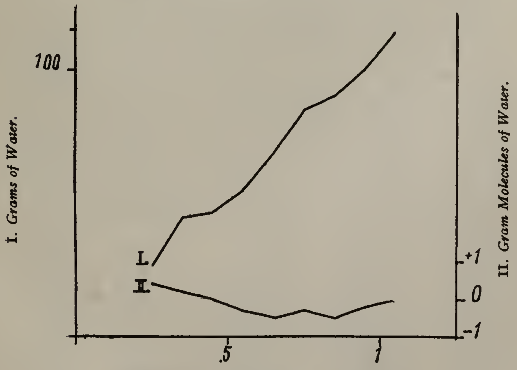
Table LXXII.—Sodium Bromide in Mixture of Lithium Bromide and Sodium Bromide.

m.	D_{H_2O}.	D_m.	*m.*	D_{H_2O}.	D_m.
0.25	54	0.7	0.75	180	—1.1
0.35	72	0.2	0.85	205	—0.2
0.45	104	0.2	0.95	222	—0.1
0.55	134	—0.1	1.05	236	0.0
0.65	159	—0.2			

These values are plotted as curves in Figs. XI. and XII. The fact that the curves show positive values of D_m has already been explained as probably due to the increased hydrating power of the molecule over its ions, so that when sufficient driving back in dissociation occurs we would get an increased amount of water eliminated as water of hydration. That this difference is nearly constant is to be expected, since corresponding additions of sodium bromide and lithium bromide are always made in changes of concentration.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Lithium Bromide and in the Mixture of Lithium Bromide and Sodium Bromide.*

II. *Differences between the Values of M for Lithium Bromide in Single Solution and in the Mixture of Lithium Bromide and Sodium Bromide.*



Gram Molecules of Salt per Liter of Solution.

Fig. XI.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Sodium Bromide and in the Mixture of Sodium Bromide and Lithium Bromide.*

II. *Difference between the Values of M for Sodium Bromide in Single Solution and in the Mixture of Sodium Bromide and Lithium Bromide.*

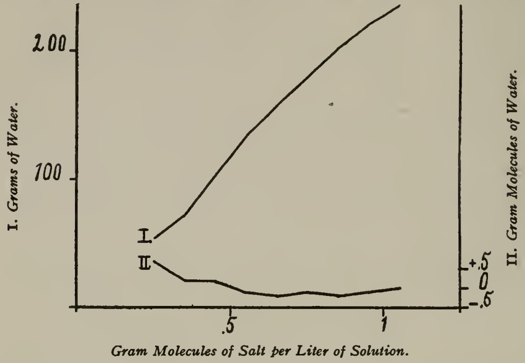


Fig. XII.

We next consider a mixture of calcium nitrate and magnesium nitrate, both of which have hydrating power.

CALCIUM NITRATE.

Table LXXIII.—Freezing Point Measurements.

m.	Δ.	Δ/*m*.	*m.*	Δ.	Δ/*m*.
0.25	1°.189	4.756	1.05	5°.123	4.88
0.45	2°.094	4.65	1.25	6°.345	5.08
0.65	3°.041	4.68	1.45	7°.547	5.21
0.85	4°.057	4.77	1.6555	8°.859	5.35

Table LXXIV.—Conductivity Measurements.

m.	*V.*	*k.*	Λ*v*.	α.
0.25	4.0000	0.020975	83.9	0.624
0.45	2.2222	0.033259	73.9	0.550
0.65	1.5380	0.042932	66.0	0.491
0.85	1.1765	0.050272	59.2	0.440
1.15	0.9525	0.056301	53.6	0.399
1.25	0.8000	0.060363	48.3	0.359
1.45	0.6897	0.063236	43.6	0.324
1.6555	0.6041	0.064674	39.1	0.291

Table LXXV.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.77665	1.0260	24.7405	1.0
0.45	26.3748	1.8467	24.5281	1.9
0.65	26.9693	2.6674	24.3019	2.8
0.85	27.5168	3.4882	24.2860	3.9
1.05	28.1060	4.3089	23.7971	4.8
1.25	28.6822	5.1297	23.5525	5.8
1.45	29.2340	5.9504	23.2836	6.9
1.6555	29.8480	6.7938	23.0542	7.8

Table LXXVI.—Hydrates.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.25	0.624	4.18	4.76	4.71	6.3	25.2
0.45	0.550	3.90	4.65	4.56	8.0	17.9
0.65	0.491	3.69	4.68	4.55	10.5	16.2
0.85	0.440	3.50	4.77	4.58	13.1	15.4
1.05	0.391	3.34	4.88	4.65	15.7	15.0
1.25	0.359	3.20	5.08	4.79	18.4	14.7
1.45	0.324	3.07	5.21	4.85	20.4	14.1
1.6555	0.291	2.94	5.35	4.93	22.4	13.5

MAGNESIUM NITRATE.

Table LXXVII.—Freezing Point Measurements.

m.	Δ.	Δ/m.	m.	Δ.	Δ/m.
0.25	1°.252	5.01	1.05	6°.762	6.44
0.45	2°.395	5.32	1.25	8°.562	6.85
0.65	3°.669	5.64	1.45	10°.589	7.30
0.85	5°.113	6.02			

Table LXXVIII.—Conductivity Measurements.

$\Lambda_\infty\ 0° = 128.5.$

m.	V.	k.	Λv.	α.
0.25	4.0000	0.021563	86.3	0.671
0.45	2.2222	0.035123	78.1	0.607
0.65	0.5380	0.046942	72.2	0.562
0.85	1.1765	0.056821	66.9	0.520
1.05	0.9525	0.065334	62.2	0.484
1.25	0.8000	0.071668	57.3	0.446
1.45	0.68966	0.076279	52.6	0.409

Table LXXIX.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.25	25.6880	0.9277	24.7603	1.0
0.45	26.2075	1.6699	24.5376	1.8
0.65	26.7605	2.4122	24.3483	2.6

Table LXXIX.—(Continued).

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.85	27.1958	3.1543	24.0415	3.8
1.05	27.7080	3.8965	23.8115	4.8
1.25	28.2435	4.6287	23.6048	5.6
1.45	28.7626	5.3809	23.3817	6.5

Table LXXX.—Hydrates.

m.	*α.*	*L.*	*Δ/m.*	*L′.*	*M.*	*H.*
0.25	0.671	4.36	5.01	4.96	6.7	26.8
0.45	0.607	4.12	5.32	5.22	11.7	26.0
0.65	0.562	3.95	5.64	5.49	15.6	24.0
0.85	0.520	3.80	6.02	5.79	19.1	22.5
1.05	0.484	3.66	6.44	6.13	22.4	21.3
1.25	0.446	3.52	6.85	6.47	25.3	20.2
1.45	0.409	3.38	7.30	6.83	28.1	19.4

Data for the *mixture* of calcium nitrate and magnesium nitrate follow:

Table LXXXI.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.5 $Ca(NO_3)_2$	1	2°.498	2.1 $Ca(NO_3)_2$	1	19°.90
0.5 $Mg(NO_3)_2$	1		2.1 $Mg(NO_3)_2$	1	
0.9 $Ca(NO_3)_2$	1	4°.856	2.5 $Ca(NO_3)_2$	1	19°.73
0.9 $Mg(NO_3)_2$	1		2.5 $Mg(NO_3)_2$	1	
1.3 $Ca(NO_3)_2$	1	7°.624	2.9 $Ca(NO_3)_2$	1	24°.8
1.3 $Mg(NO_3)_2$	1		2.9 $Mg(NO_3)_2$	1	
1.7 $Ca(NO_3)_2$	1	10°.93			
1.7 $Mg(NO_3)_2$	1				

Table LXXXII.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.5 $Ca(NO_3)_2$	1	26.4387	1.9537	24.4850	2.1
0.5 $Mg(NO_3)_2$	1				
0.9 $Ca(NO_3)_2$	1	27.5300	3.5166	24.0134	3.9
0.9 $Mg(NO_3)_2$	1				
1.3 $Ca(NO_3)_2$	1	28.5974	5.0796	23.5178	5.9
1.3 $Mg(NO_3)_2$	1				
1.7 $Ca(NO_3)_2$	1	29.6600	6.6425	23.0175	7.9
1.7 $Mg(NO_3)_2$	1				
2.1 $Ca(NO_3)_2$	1	30.6253	8.2055	22.4198	10.3
2.1 $Mg(NO_3)_2$	1				
2.5 $Ca(NO_3)_2$	1	31.6538	9.7684	21.8854	12.5
2.5 $Mg(NO_3)_2$	1				
2.9 $Ca(NO_3)_2$	1	32.6175	11.3313	21.2862	14.9
2.9 $Mg(NO_3)_2$	1				

Table LXXXIII.—Conductivity Measurements.

m.	P.	m_c.	V_c.	k_u.	k.	D.	k_c.	Λ_v.	α.
0.5 $Ca(NO_3)_2$	1	0.25	4.0000	0.036833	0.020795	0.003705	0.019013	76.1	0.565
0.5 $Mg(NO_3)_2$	1	0.25	4.0000		0.021563		0.019820	79.3	0.671
0.9 $Ca(NO_3)_2$	1	0.45	2.2222	0.054700	0.033259	0.013682	0.025920	57.6	0.428
0.9 $Mg(NO_3)_2$	1	0.45	1.2222		0.035123		0.028780	64.0	0.498
1.3 $Ca(NO_3)_2$	1	0.65	1.538	0.065970	0.042932	0.023904	0.029904	46.0	0.342
1.3 $Mg(NO_3)_2$	1	0.65	1.538		0.046942		0.036066	55.5	0.432
1.7 $Ca(NO_3)_2$	1	0.85	1.1765	0.071201	0.050272	0.035892	0.030420	35.8	0.266
1.7 $Mg(NO_3)_2$	1	0.85	1.1765		0.056821		0.040781	48.0	0.373
2.1 $Ca(NO_3)_2$	1	1.05	0.9523	0.071673	0.056301	0.049962	0.028332	27.0	0.201
2.1 $Mg(NO_3)_2$	1	1.05	0.9523		0.065334		0.043341	41.3	0.321
2.5 $Ca(NO_3)_2$	1	1.25	0.8000	0.069140	0.060363	0.062891	0.024807	19.9	0.148
2.5 $Mg(NO_3)_2$	1	1.25	0.8000		0.071668		0.044433	35.5	0.276
2.9 $Ca(NO_3)_2$	1	1.45	0.68966	0.063327	0.063236	0.076188	0.019866	13.7	0.102
2.9 $Mg(NO_3)_2$	1	1.45	0.68966		0.076279		0.043461	30.0	0.233

Table LXXXIV.—Hydrates.

P equals 1 in each case.

m.	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Hc.*	*Mc.*
0.5 $Ca(NO_3)_2$	0.25	0.565	3.96	6.3	2.498	2.1	4.6	18.5
0.5 $Mg(NO_3)_2$	0.25	0.617	4.16	6.7			5.2	20.8
0.9 $Ca(NO_3)_2$	0.45	0.428	3.45	8.0	4.856	3.9	7.2	16.0
0.9 $Mg(NO_3)_2$	0.45	0.498	3.71	11.7			11.1	24.7
1.3 $Ca(NO_3)_2$	0.65	0.342	3.13	10.5	7.624	5.9	9.4	14.4
1.3 $Mg(NO_3)_2$	0.65	0.432	3.47	15.6			14.9	22.9
1.7 $Ca(NO_3)_2$	0.85	0.266	2.85	13.1	10.93	7.9	11.7	13.8
1.7 $Mg(NO_3)_2$	0.85	0.373	3.25	19.1			18.1	21.3
2.1 $Ca(NO_3)_2$	1.05	0.201	2.61	15.7	14.90	10.3	13.6	13.0
2.1 $Mg(NO_3)_2$	1.05	0.321	3.05	22.4			21.0	20.0
2.5 $Ca(NO_3)_2$	1.25	0.148	2.41	18.4	19.73	12.5	15.7	12.5
2.5 $Mg(NO_3)_2$	1.25	0.276	2.89	25.3			23.3	18.7
2.9 $Ca(NO_3)_2$	1.45	0.102	2.24	20.4	24.8	14.9	16.5	11.4
2.9 $Mg(NO_3)_2$	1.45	0.233	2.73	28.1			25.2	17.4

I. *Magnesium Nitrate Alone.*
II. *Magnesium Nitrate Mixed with Calcium Nitrate.*
III. *Calcium Nitrate Alone.*
IV. *Calcium Nitrate Mixed with Magnesium Nitrate.*

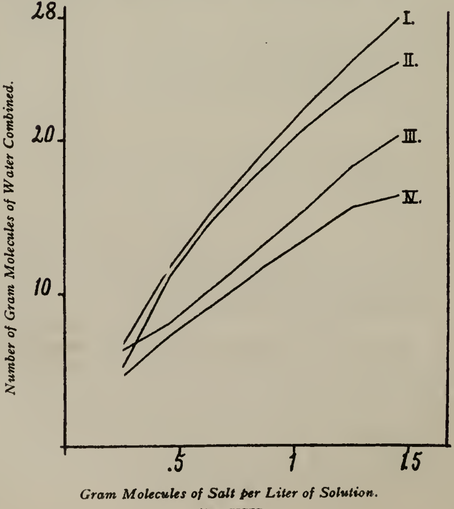


Fig. XIII.

The values of M for each salt in the mixture and in separate solution are plotted as curves in Fig. XIII. With increased concentration we have increased divergence in curves I. and III., which represent the hydrating power (values of M) in separate solutions of magnesium nitrate and of calcium nitrate, respectively. Consequently, as we should expect, curves II. and IV., representing the values of M for the two salts in the mixture, show increasing divergence with increase in concentration.

Table LXXXV.—Calcium Nitrate in Mixture of Calcium Nitrate and Magnesium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	104.4	1.7	1.05	432.5	2.1
0.45	220.3	0.8	1.25	487.0	2.7
0.65	298.5	1.1	1.45	534.0	3.9
0.85	365.7	1.4			

Table LXXXVI.—Magnesium Nitrate in Mixture of Calcium Nitrate and Magnesium Nitrate.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	93.7	1.5	1.05	300	1.4
0.45	150.5	0.6	1.25	351	2.0
0.65	202.0	0.7	1.45	381	2.9
0.85	251.0	1.0			

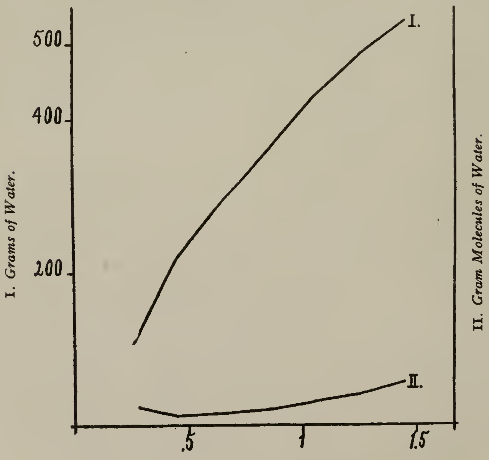
These values are plotted as curves in Figs. XIV. and XV.

The curves in Figs. XIV. and XV. show the same general relations as the preceding curves of the same character, excepting those of lithium bromide and sodium bromide. The amount of water eliminated to form hydrates in the mixture tends to diminish somewhat, proportionally to the diminution in the amount of water present which is acting as solvent. This is clearly shown by the direction in which the curves turn with increased concentration of the solutions. It is probable that in the more dilute solutions we have the difference in the hydrating power of the ions and molecules affecting the total amount of water eliminated as water of hydration. Consequently, where the total amount of salt is constant, but a change in the dissociation is produced, if the number of ions is large relative to the number of molecules undissociated, as is the case in the more dilute solutions, the curve for D_m does not at once show the influence of diminishing the amount of solvent present. This phenomenon is shown by the curves as change of direction, or as increased curvature in the curve which represents the value of D_m.

A pair of quarternary electrolytes was next studied. Ferric chloride and calcium chloride were employed. Very concentrated stock solutions were prepared, and the necessary measurements were made as quickly as possible, in order to

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Calcium Nitrate and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*

II. *Difference between the Values of M for Calcium Nitrate in Single Solution and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*

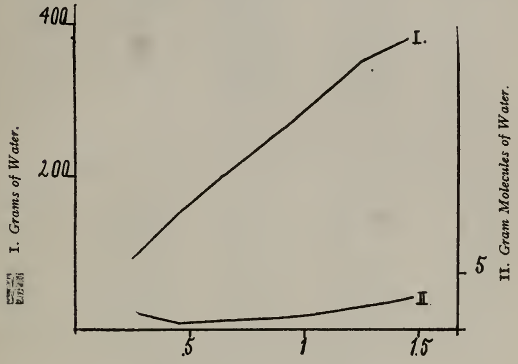


Gram Molecules of Salt per Liter of Solution.

Fig. XIV.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Magnesium Nitrate and in the Mixture of Magnesium Nitrate and Calcium Nitrate.*

II. *Difference between the Values of M for Magnesium Nitrate in Single Solution and in the Mixture of Calcium Nitrate and Magnesium Nitrate.*



Gram Molecules of Salt per Liter of Solution.

Fig. XV.

reduce hydrolysis to a minimum, there being an appreciable time factor in the hydrolysis of such compounds as ferric chloside. Notwithstanding all precautions there was, of course, conriderable hydrolysis. Especially was this the case in the mixture of the two salts, the presence of the aluminium chloride appearing to act catalytically upon the solution of ferric chloride,* causing a gradual precipitation of ferric hydroxide.

ALUMINIUM CHLORIDE.

Table LXXXVII.—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.2	1°.279	6.40	1.0	11°.795	11.80
0.4	2°.910	7.28	1.2	16°.385	13.65
0.6	5°.144	8.57	1.3617	21°.75	15.97
0.8	7°.962	9.95	1.415	23°.50	16.60

Table LXXXVIII.—Conductivity Measurements.

Λ_∞ 0° = 181.7 (Calculated from Jones and Getman's value of $\mu\infty$).

m.	*V.*	*k.*	Λv.	*α.*
0.2	5.000	0.023983	119.9	0.660
0.4	2.500	0.040530	101.3	0.558
0.6	1.6666	0.053115	88.5	0.487
0.8	1.250	0.061180	76.5	0.421
1.0	1.000	0.066595	66.6	0.367
1.2	0.8333	0.06842	57.0	0.314
1.3617	0.7344	0.06760	49.7	0.273

Table LXXXIX.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.2	25.6240	0.6673	24.9567	0.2
0.4	26.1538	1.3346	24.8192	0.7
0.6	26.7134	2.0019	24.7115	1.2
0.8	27.2153	2.6692	24.5461	1.8
1.0	27.7351	3.3365	24.3986	2.4
1.2	28.2877	4.0038	24.2839	2.9
1.3617	28.7252	4.5433	24.1819	3.3

Table XC.—Hydrates.

m.	*α.*	*L.*	Δ/*m.*	*L′.*	*M.*	*H.*
0.2	0.660	5.54	6.40	6.39	7.4	37.0
0.4	0.558	4.97	7.28	7.23	7.4	43.5
0.6	0.487	4.58	8.57	8.47	25.5	42.5
0.8	0.421	4.21	9.95	9.77	31.6	39.5
1.0	0.367	3.91	11.80	11.52	36.7	36.7
1.2	0.314	3.61	13.65	13.25	40.4	33.7
1.3617	0.273	3.39	15.97	15.44	43.4	31.9

FERRIC CHLORIDE.

Table XCI .—Freezing Point Measurements.

m.	Δ.	Δ/*m.*	*m.*	Δ.	Δ/*m.*
0.2	1°.255	6.28	1.0	9°.152	9.15
0.4	2°.715	6.79	1.2	12°.11	10.09
0.6	4°.530	7.55	1.3617	14°.592	10.72
0.8	6°.667	8.33			

Table XCII.—Conductivity Measurements.

Λ_∞ 0° = 220 (calculated).

m.	*V.*	*k.*	$\Lambda v.$	$\alpha.$
0.2	5.000	0.02380	119.0	0.541
0.4	2.500	0.03786	94.7	0.430
0.6	1.6666	0.04645	77.4	0.352
0.8	1.250	0.05147	64.3	0.292
1.0	1.000	0.053147	53.1	0.241
1.2	0.8333	0.053145	44.3	0.201
1.3617	0.7344	0.051777	38.0	0.173

Table XCIII.—Weight-Normal Corrections.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.2	25.6792	0.8113	24.8679	0.5
0.4	26.3380	1.6225	24.7155	1.1
0.6	26.9956	2.4337	24.5619	1.8
0.8	27.6230	3.2450	24.3780	2.5
1.0	28.2400	4.056	24.1840	3.3
1.2	28.8867	4.8675	24.0192	3.9
1.3617	29.3690	5.5234	23.8456	4.6

Table XCIV.—Hydrates.

m.	$\alpha.$	*L.*	$\Delta/m.$	*L′.*	*M.*	*H.*
0.2	0.541	4.88	6.28	6.25	12.2	61.0
0.4	0.430	4.26	6.79	6.72	20.3	50.7
0.6	0.352	3.82	7.55	7.41	26.9	44.8
0.8	0.292	3.49	8.33	8.12	31.7	39.6
1.0	0.241	3.21	9.15	8.85	35.4	35.4
1.2	0.201	2.98	10.09	9.70	38.5	32.1
1.3617	0.173	2.82	10.72	10.23	40.2	29.5

MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

Table XCV.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.4 $FeCl_3$	1	2°.938	2.0 $FeCl_3$	1	36°.0
0.4 $AlCl_3$	1		2.0 $AlCl_3$	1	
0.8 $FeCl_3$	1	7°.28	2.4 $FeCl_3$	1	56°.0
0.8 $AlCl_3$	1		2.4 $AlCl_3$	1	
1.2 $FeCl_3$	1	13°.69	2.7234 $FeCl_3$	1	84°.6
1.2 $AlCl_3$	1		2.7234 $AlCl_3$	1	
1.6 $FeCl_3$	1	22°.5			
1.6 $AlCl_3$	1				

It was necessary to extrapolate this last value, 84°.6, since the solution failed to freeze in the freezing mixture employed, *i. e.*, solid carbon dioxide and alcohol. The more concentrated solutions became so viscous, when cooled down, that it was difficult to stir them properly.

Table XCVI.—Weight-Normal Corrections.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.4 $FeCl_3$	1	26.2807	1.4786	24.8021	0.8
0.4 $AlCl_3$	1				
0.8 $FeCl_3$	1	27.4365	2.9571	24.4794	2.1
0.8 $AlCl_3$	1				
1.2 $FeCl_2$	1	28.5660	4.4356	24.1304	3.5
1.2 $AlCl_3$	1				
1.6 $FeCl_3$	1	29.7105	5.9142	23.7963	4.8
1.6 $AlCl_3$	1				
2.0 $FeCl_3$	1	30.8182	7.3925	23.4257	6.3
2.0 $AlCl_3$	1				
2.4 $FeCl_3$	1	31.9182	8.8713	23.0469	7.8
2.4 $AlCl_3$	1				
2.72 $FeCl_3$	1	32.7777	10.0667	22.7110	9.2
2.72 $AlCl_3$	1				

It is to be noted that the conductivity measurements which are given in the following table are the merest approximations to measurements of dissociation. The conductivity measurements are made at zero, whereas some of these mixtures freeze very considerably below 0° C. There is marked hydrolysis in some cases, as already mentioned, leading to a precipitation of the iron. There is considerable difference between the viscosity of the single solutions and of the mixtures where the normalities are the same. The assumption that these salts dissociate at once, in the most concentrated solutions, into $\overset{+++}{M}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, is certainly not correct. Finally, the values of Λ_∞ are obtained by calculation, and may differ considerably from the true values because of the factors just mentioned.

Table XCVII.—Conductivity Measurements.

m.	P.	mc.	Vc.	k_u.	k.	D.	kc.	Λv.	α.
0.4 $FeCl_3$	1	0.2	5.000	0.040318	0.02380	0.007465	0.01935	96.8	0.440
0.4 $AlCl_3$	1	0.2	5.000		0.023983		0.020968	104.8	0.577
0.8 $FeCl_3$	1	0.4	2.500	0.060462	0.03786	0.017928	0.026928	67.3	0.306
0.8 $AlCl_3$	1	0.4	2.500		0.04053		0.033534	83.7	0.461
1.2 $FeCl_3$	1	0.6	1.6666	0.055874	0.04645	0.043691	0.019059	31.8	0.144
1.2 $AlCl_3$	1	0.6	1.6666		0.053115		0.036815	61.4	0.338
1.6 $FeCl_3$	1	0.8	1.250	0.056904	0.05147	0.055750	0.016040	20.1	0.091
1.6 $AlCl_3$	1	0.8	1.250		0.06118		0.040860	51.1	0.281
2.0 $FeCl_3$	1	1.0	1.00	0.047916	0.053147	0.071826	0.006597	6.6	0.030
2.0 $AlCl_3$	1	1.0	1.00		0.066595		0.041319	41.3	0.227
2.4 $FeCl_3$	1	1.2	0.8333	0.037866	0.053145	0.083699	0.00000	00.0	0.000
2.4 $AlCl_3$	1	1.2	0.8333		0.06842		0.03787	31.6	0.174
2.72 $FeCl_3$	1	1.3617	0.7344	0.029595	0.051777	0.089782	0.00000	00.0	0.000
2.72 $AlCl_3$	1	1.3617	0.7344		0.06760		0.029595	21.7	0.120

Table XCVIII.—Hydrates.

P equals 1 in each case.

m.	*mc.*	*α.*	*Lc.*	*M.*	Δ.	Sp. Gr. Cor.	*Mc.*	*Hc.*
0.4 $FeCl_3$	0.2	0.440	4.31	12.2	2.938	0.8	13.5	67.5
0.4 $AlCl_3$	0.2	0.577	5.08	7.4			8.2	41.0
0.8 $FeCl_3$	0.4	0.306	3.57	20.3	7.288	2.1	19.6	49.0
0.8 $AlCl_3$	0.4	0.461	4.44	17.4			16.6	41.5
1.2 $FeCl_3$	0.6	0.144	2.67	26.9	13.69	3.5	25.8	43.0
1.2 $AlCl_3$	0.6	0.338	3.74	25.5			24.4	40.7
1.6 $FeCl_3$	0.8	0.091	2.37	31.7	22.5	4.8	29.0	36.2
1.6 $AlCl_3$	0.8	0.281	3.43	31.6			28.9	36.1
2.0 $FeCl_3$	1.0	0.030	2.03	35.4	36.0	6.3	32.2	32.2
2.0 $AlCl_3$	1.0	0.227	3.02	36.7			33.7	33.7
2.4 $FeCl_3$	1.2	0.000	1.86	38.5	56.0	7.8	34.6	28.8
2.4 $AlCl_3$	1.2	0.174	2.83	40.4			36.7	30.6
2.7234 $FeCl_3$	1.3617	0.000	1.86	40.2	84.6	9.2	36.1	26.5
2.7234 $AlCl_3$	1.3617	0.120	2.53	43.4			39.6	29.0

These values of *M* and of M_c are plotted as curves in Fig. XVI. The general relation shown by these curves are the same as have previously been pointed out. The fact that the hydrating power of both the aluminium chloride and the ferric chloride is apparently greater in the mixture than in the separate solutions, in the most dilute solutions employed, is probably due to the effect of hydrolysis in increasing the value of *L*, and consequently diminishing *M*, though it may possibly be due, in part, to change in dissociation and difference in the hydrating power of the ions and molecules. It should be noted, also, that the hydrating power of the aluminium chloride appears to be relatively less than that of the ferric chloride in the more dilute solutions, but that this relation is reversed in the more concentrated solutions. This may be due to hydrolysis, since, if the aluminium chloride hydrolyzes more rapidly than the ferric chloride, then, in the more dilute solutions, where the effects of hydrolysis would be pronounced, the result would be to increase the value of *L* and, consequently, to diminish the value of *M*, based upon it.

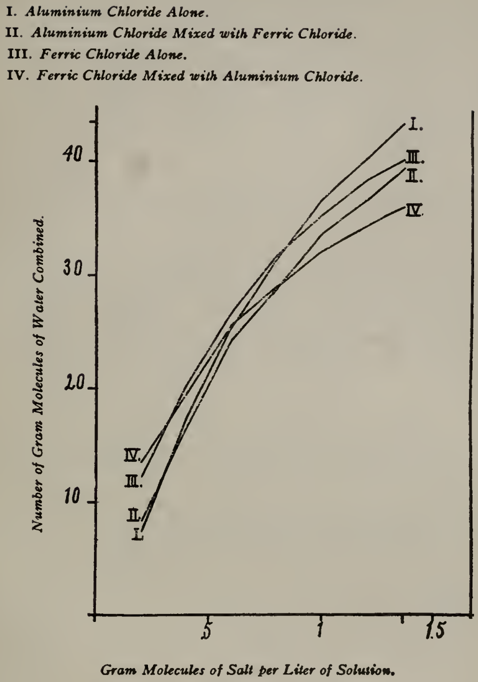


Fig. XVI.

In Tables XCIX. and C. the abbreviations have the usual significance.

Table XCIX.—Aluminium Chloride in Mixture of Aluminium Chloride and Ferric Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.2	367	—0.8	1.0	618	3.0
0.4	249	0.8	1.2	671	3.7
0.6	488	1.1	1.3617	709	3.8
0.8	552	2.7			

Table C.—Ferric Chloride in Mixture of Aluminium Chloride and Ferric Chloride.

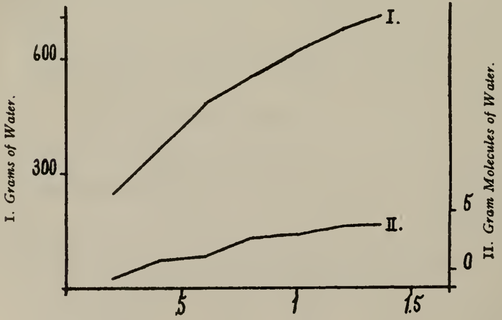
m.	D_{H_2O}.	D_m.	*m*.	D_{H_2O}.	D_m.
0.2	150	−1.3	1.0	636	3.2
0.4	308	0.7	1.2	699	3.9
0.6	456	1.1	1.3617	758	4.1
0.8	543	2.7			

These values are plotted as curves in Figs. XVII. and XVIII.

The effect of decrease in the amount of water present as solvent is plainly shown in the diminishing values of *M* as the amount of solvent is lessened. The slight irregularities are probably due to unavoidable experimental error, and inaccuracy of the conductivity method as a measure of dissociation.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Aluminium Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.*

II. *Difference between the Values of M for Aluminium Chloride in Single Solution and in the Mixture of Aluminium Chloride and Ferric Chloride.*

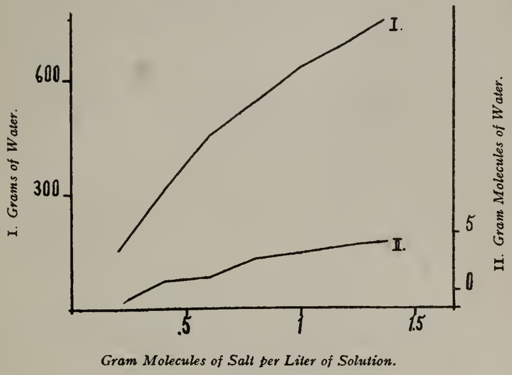


Gram Molecules of Salt per Liter of Solution.

Fig. XVII.

I. *Difference between the Amount of Water Present as Solvent in the Single Solution of Ferric Chloride and in the Mixture of Ferric Chloride and Aluminium Chloride.*

II. *Difference between the Values of M for Ferric Chloride in Single Solution and in the Mixture of Ferric Chloride and Aluminium Chloride.*



XVIII.

Thus far all of the salts studied have a common anion. In order to extend the investigation to a pair of salts having a common cation, a mixture of calcium nitrate and calcium chloride was employed.

The data for the separate solutions of these two salts has already been given. The results obtained with the mixture follow:

Table CI.—Freezing Point Measurements.

m.	*P.*	Δ.	*m.*	*P.*	Δ.
0.5 $Ca(NO_3)_2$	1	2°.50	2.1 $Ca(NO_3)_2$	1	14°.78
0.5 $CaCl_2$	1		2.1 $CaCl_2$	1	
0.9 $Ca(NO_3)_2$	1	4°.88	2.5 $Ca(NO_3)_2$	1	19°.2
0.9 $CaCl_2$	1		2.5 $CaCl_2$	1	
1.3 $Ca(NO_3)_2$	1	7°.67	2.9 $Ca(NO_3)_2$	1	24°.2
1.3 $CaCl_2$	1		2.9 $CaCl_2$	1	
1.7 $Ca(NO_3)_2$	1	11°.00	3.31102 $Ca(NO_3)_2$	1	30°.7
1.7 $CaCl_2$	1		3.31102 $CaCl_2$	1	

Table CII.—Conductivity Measurements.

m.	P.	mc.	Vc.	ku.	k.	D.	kc.	Λv.	α.
0.5 $Ca(NO_3)_2$	1	0.25	4.0000	0.039475	0.020975	0.055730	0.018254	73.0	0.543
0.5 $CaCl_2$	1	0.25	4.0000		0.024073		0.021221	84.9	0.575
0.9 $Ca(NO_3)_2$	1	0.45	2.2222	0.059937	0.032590	0.013010	0.026780	59.5	0.442
0.9 $CaCl_2$	1	0.45	2.2222		0.039688		0.033157	73.7	0.499
1.3 $Ca(NO_3)_2$	1	0.65	1.5380	0.073550	0.042632	0.023618	0.030833	47.4	0.353
1.3 $CaCl_2$	1	0.65	1.5380		0.054236		0.042716	65.7	0.445
1.7 $Ca(NO_3)_2$	1	0.85	1.1765	0.081797	0.050272	0.035378	0.031691	37.3	0.277
1.7 $CaCl_2$	1	0.85	1.1765		0.066903		0.050106	59.0	0.400
2.1 $Ca(NO_3)_2$	1	1.05	0.9523	0.084100	0.056301	0.050445	0.029266	27.9	0.207
2.1 $CaCl_2$	1	1.05	0.9523		0.078344		0.054834	52.2	0.354
2.5 $Ca(NO_3)_2$	1	1.25	0.8000	0.068281	0.060363	0.066535	0.023751	19.0	0.141
2.5 $CaCl_2$	1	1.25	0.8000		0.088853		0.058930	47.1	0.320
2.9 $Ca(NO_3)_2$	1	1.45	0.68966	0.077154	0.063236	0.083467	0.016375	11.3	0.084
2.9 $CaCl_2$	1	1.45	0.68966		0.097385		0.060780	41.9	0.284
3.311 $Ca(NO_3)_2$	1	1.6555	0.60405	0.069853	0.064674	0.098121	0.008650	5.2	0.039
3.311 $CaCl_2$	1	1.6555	0.60405		0.003300		0.061203	37.0	0.251

Table CIII.—Weight-Normal Corrections.

m.	*P.*	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction, per cent.
0.5 $Ca(NO_3)_2$	1	26.3336	1.7197	24.6139	1.5
0.5 $CaCl_2$	1				
0.9 $Ca(NO_3)_2$	1	27.3415	3.0954	24.2461	3.0
0.9 $CaCl_2$	1				
1.3 $Ca(NO_3)_2$	1	28.3615	4.4711	23.8904	4.4
1.3 $CaCl_2$	1				
1.7 $Ca(NO_3)_2$	1	29.3082	5.8469	23.4613	6.2
1.7 $CaCl_2$	1				
2.1 $Ca(NO_3)_2$	1	30.2933	7.3260	23.0707	7.7
2.1 $CaCl_2$	1				
2.5 $Ca(NO_3)_2$	1	31.2197	8.5984	22.6213	9.5
2.5 $CaCl_2$	1				
2.9 $Ca(NO_3)_2$	1	32.1762	9.9741	22.2021	11.2
2.9 $CaCl_2$	1				
3.311 $Ca(NO_3)_2$	1	33.0792	11.3878	21.6914	13.2
3.311 $CaCl_2$	1				

Table CIV.—Hydrates.

P equals 1 in each case.

m.	m_c.	α.	L_c.	*M.*	Δ.	Sp. Gr. Cor.	M_c.	H_c.
0.5 $Ca(NO_3)_2$	0.25	0.543	3.88	6.3	2.50	1.5	4.6	18.4
0.5 $CaCl_2$	0.25	0.575	4.00	8.2			7.0	28.0
0.9 $Ca(NO_3)_2$	0.45	0.442	3.51	8.0	4.88	3.0	7.4	16.4
0.9 $CaCl_2$	0.45	0.499	3.72	11.7			11.2	24.9
1.3 $Ca(NO_3)_2$	0.65	0.353	3.17	10.5	7.67	4.4	9.5	14.8
1.3 $CaCl_2$	0.65	0.445	3.52	15.7			15.1	23.2
1.7 $Ca(NO_3)_2$	0.85	0.277	2.89	13.1	11.00	6.2	12.1	14.2
1.7 $CaCl_2$	0.85	0.400	3.35	18.9			18.2	21.4
2.1 $Ca(NO_3)_2$	1.05	0.207	2.63	15.7	14.78	7.7	14.1	13.4
2.1 $CaCl_2$	1.05	0.354	3.18	21.9			20.8	19.8
2.5 $Ca(NO_3)_2$	1.25	0.141	2.39	18.4	19.20	9.5	16.4	13.1
2.5 $CaCl_2$	1.25	0.320	3.05	24.3			22.8	18.2
2.9 $Ca(NO_3)_2$	1.45	0.084	2.17	20.4	24.2	11.2	17.6	12.1
2.9 $CaCl_2$	1.45	0.284	2.92	27.3			25.2	17.4
3.311 $Ca(NO_3)_2$	1.6555	0.039	2.01	22.4	30.7	13.2	16.4	9.9
3.311 $CaCl_2$	1.6555	0.251	2.79	30.1			25.6	15.5

The above values of *M* are plotted as curves in Fig. XIX. The results are of the same character as those shown by the preceding mixtures. The most concentrated solution measured shows a somewhat lower value for *M* in the mixture than we should expect, but it must be borne in mind that at this great concentration the experimental errors involved are necessarily very large.

I. *Calcium Chloride Alone.*
II. *Calcium Chloride Mixed with Calcium Nitrate.*
III. *Calcium Nitrate Alone.*
IV. *Calcium Nitrate Mixed with Calcium Chloride.*

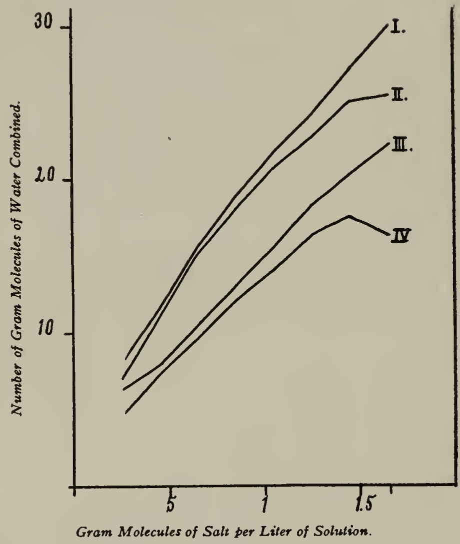


Fig. XIX.

Tables CV. and CVI. contain the data necessary to compare the change in the amount of solvent present with the change in the values of *M* in separate solution and in the mixture.

Table CV.—Calcium Chloride in Mixture of Calcium Nitrate and Calcium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	92	1.2	1.05	306	1.1
0.45	153	0.5	1.25	358	1.5
0.65	202	0.6	1.45	392	2.1
0.85	260	0.7	0.65555	386	4.5

Table CVI.—Calcium Nitrate in Mixture of Calcium Nitrate and Calcium Chloride.

m.	D_{H_2O}.	D_m.	m.	D_{H_2O}.	D_m.
0.25	131	1.7	1.05	404	1.6
0.45	213	0.6	1.25	447	2.0
0.65	288	0.9	1.45	496	2.8
0.85	350	1.0	1.6555	575	6.0

These values are plotted as curves in Figs. XX. and XXI. A diminution in the amount of water present as solvent causes a diminution in the value of M. This effect appears to be greater with increasing concentration. It is probable that in the most dilute solutions the difference in the hydrating power of the ions and molecules affects the curve, changing its direction.

I. *Difference between the Amount of Water acting as Solvent toward the Calcium Nitrate in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Nitrate.*

II. *Difference between the Values of M for Calcium Nitrate in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.*

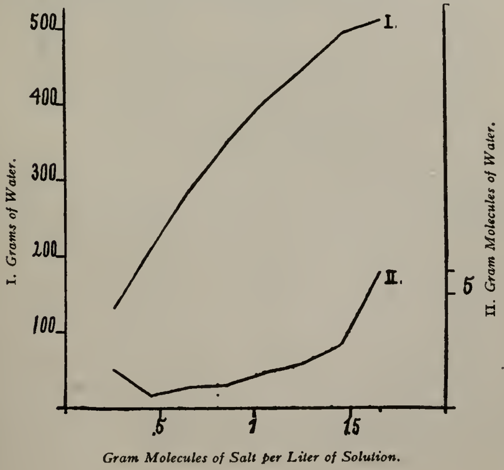
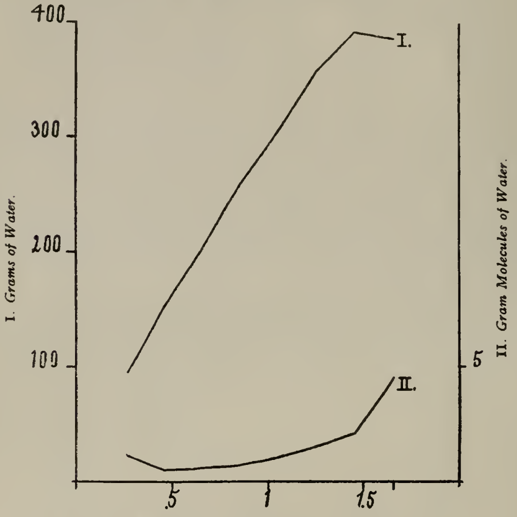


Fig. XX.

I. *Difference between the Amount of Water acting as Solvent toward the Calcium Chloride in the Mixture of Calcium Nitrate and Calcium Chloride and in the Separate Solution of Calcium Chloride.*

II. *Difference between the Values of M for Calcium Chloride in Separate Solution and in the Mixture of Calcium Nitrate and Calcium Chloride.*



Gram Molecules of Salt per Liter of Solution.
Fig. XXI.

THE EFFECT OF CHANGE IN TEMPERATURE ON THE CONDUCTIVITIES OF SEPARATE SOLUTIONS OF ELECTROLYTES AND ON MIXTURES OF THESE ELECTROLYTES.

In this paper we have repeatedly called attention to the fact that the conductivity method furnishes us with only an approximate value of the dissociation of a salt. The conductivity method of measuring dissociation is, however, the most general one available. In order to study the effect of change of temperature upon the conductivities of separate solutions of electrolytes and upon mixtures of these electrolytes, it was necessary *to select a pair of salts which do not* *form double salts in solution and which have little or no hydrating power. Potassium chloride and ammonium chloride were used.*

The conductivities of single solutions of these salts and of their mixture were studied at 0° and 12°. Comparisons having shown that our values agree very closely with those obtained by Jones and West[1] and by Jones and Knight,[2] the values of Jones and Knight, at 25°, were used. The values of Jones and West, at 18°, show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature. The values for potassium chloride at 25° are taken from the results of Kohlrausch.

POTASSIUM CHLORIDE.

Table CVII.—Molecular Conductivities.

V.	μ 0°.	μ 12°.	*V.*	μ_v 25°.
1	61.58	82.05	1	104.1
2	63.02	84.43	2	108.6
5	65.85	87.84	4	111.2
20	68.59	92.88	16	121.5
100	72.13	98.69	80	128.5
200	73.73	101.3	160	131.1
1000	74.31	103.3	640	133.9

AMMONIUM CHLORIDE.

Table CVIII.—Molecular Conductivities.

V.	μ_v 0°.	μ_v 12°.	*V.*	μ_v 25°.
1	61.08	81.15	1	99.3
2	62.53	83.57	2	104.9
5	63.98	87.66	4	110.4
20	68.13	93.19	16	120.9
100	71.64	99.94	80	131.8
200	72.89	101.3	160	134.2
1000	74.10	103.7	640	138.1

Since we are employing some of the values of Jones and West, Jones and Knight, and Kohlrausch, at 25°, we have tabulated a few values taken from these sources side by side with our own.

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[1] This Journal, **34**, 381 (1905).

[2] *Ibid.*, **22**, 125 (1899).

POTASSIUM CHLORIDE.

Table CIX.—Comparison of Conductivities.

	Jones and Stine.	Jones and West.	Jones and West.	Kohlrausch.
V.	μ_v 0°.	μ_v 0°.	μ_v 18°.	μ_v 18°.
1	61.58	...	...	...
2	63.02	62.96	95.9	95.8
5	65.85	...	...	...
8	...	66.47	103.6	...
16	...	68.40	107.0	...
20	68.59	...	...	108.3
32	...	70.27	110.7	...
120	72.13	...	...	114.7
128	...	73.00	115.5	...
200	73.73	...	...	....
1000	74.31	....	...	119.3
1024	...	75.14	119.3	...

AMMONIUM CHLORIDE.

Table CX.—Comparison of Conductivities.

	Jones and Stine.	Jones and West.	Jones and West.	Kohlrausch.
V.	μ_v 0°.	μ_v 0°.	μ_v 18°.	μ_v 18°.
1	61.08	...	...	...
2	62.53	62.76	96.3	94.8
5	63.98	....	...	...
8	...	66.17	103.6	...
16	...	68.02	107.2	...
20	68.13	...	...	107.8
32	...	70.2	110.8	...
100	71.64	...	...	114.2
128	...	73.08	...	...
200	72.89	...	116.2	...
1000	74.10	...	...	119.0
1024	...	74.84	119.6	...

Table CXI.—Comparison of Conductivities.

	Jones and West.			Jones and Knight.	
V.	μ_v 25°	μ_v 25°	*V.*	μ_v 25°	μ_v 25°.
1	...	99.3	160	...	134.2
2	109.2	104.9	512	136.8	...
8	118.6	115.8	640	...	138.1
16	123.2	120.9	1024	137.8	...
32	127.6	125.3	1600	...	138.9
128	133.4	...			

In connection with the conductivity of ammonium chloride, Jones and Knight say:[1] "The values which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch,[2] our values being somewhat lower in the more concentrated solutions, and a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values, to transform them from 18° to 25°." This coefficient was uncertain over any considerable range of temperature.

POTASSIUM CHLORIDE.

Table CXII.—Comparison of Conductivities.

V.	Jones and West. μ_v 25°.	Jones and Knight. (Kohlrausch). μ_v 25°.	*V.*	Jones and West. μ_v 25°.	Jones and Knight. (Kohlrausch). μ_v 25°.
1	...	104.5	160	...	131.1
2	109.5	108.6	512	135.5	...
8	118.6	116.5	640	...	133.9
16	122.9	121.5	1024	137.0	...
32	126.8	125.4	1600	...	135.4
128	132.4	...			

From these tables it is evident that our values agree very well with those of Kohlrausch, Jones and West, and Jones and Knight.

Let us turn, now, to the conductivities of the mixtures of potassium chloride and ammonium chloride. These solutions were mixed in equal volumes. When, for example, a 2.0 N solution of potassium chloride is added to an equal volume of 2.0 N ammonium chloride, the assumption that the resulting solution consists of 1.0 N potassium chloride and 1.0 N ammonium chloride is evidently not quite correct, because of the volume occupied by the salt in the added solution. In order to make the necessary correction for this factor, pycnometer measurements were made with the more concentrated solutions. In the more dilute solutions this factor is so small that it is entirely negligible.

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[1] This Journal, **22**, 117 (1899).

[2] Wied. Ann., **26**, 161.

In the following table, m is the normality; C is the capacity of the pycnometer in cubic centimeters; W_{Salt} is the weight of salt present in the solution; W_{H_2O} is the weight of water present in the volume of solution contained in the pycnometer; and v is the volume of water in a thousand cubic centimeters of the solution.

Table CXIII.—Potassium Chloride, at 12°.

m.	C.	W_{Salt}.	W_{H_2O}.	V.
0.05	24.4259	0.0911	24.3821	998.66
0.20	23.9474	0.35373	23.8077	994.62
0.50	11.6945	0.4362	11.5294	986.35
1.00	12.6976	0.9472	12.3370	972.16

Table CXIV.—Ammonium Chloride, at 12°.

m.	C.	W_{Salt}.	W_{H_2O}.	V.
0.2	24.3605	0.2608	24.1679	992.54
0.4	24.4259	0.5229	24.0573	985.37
0.6	23.9474	0.7690	23.4098	978.00
0.8	12.6976	0.5437	12.3176	970.52
1.0	11.6945	0.6259	11.2574	963.07

Based upon these measurements, the conductivity of the potassium chloride and ammonium chloride in the various mixtures was calculated, on the assumption that no change in the dissociation of these salts takes place when their solutions are mixed. The results are given, along with the conductivities of the mixtures, in the following tables:

Table CXV.—Comparison for Potassium Chloride, Ammonium Chloride.

V.	KCl μv 25°.	V.	NH_4Cl μv 25°.	Sum.	V.	$KCl + NH_4Cl$ μv 25°.	Difference.
1	104.1	1	99.3	203.4	1	179.3	24.1
2	108.6	2	104.9	213.5	2	195.0	18.5
4	111.2	4	110.4	221.6	4	208.3	13.3
8	116.5	8	115.8	232.3	8	220.9	11.4
16	121.5	16	120.9	242.4	16	231.7	10.7
32	125.4	32	125.3	250.7	32	241.2	9.5
40	125.7	40	127.6	253.3	40	245.9	7.4
80	128.5	80	131.8	260.3	80	254.3	6.0
160	131.1	160	134.2	265.3	160	263.3	3.0
320	132.1	320	136.8	268.9	320	267.0	1.9
640	133.9	640	138.1	272.0	640	273.1	—1.1
1600	135.4	1600	138.9	274.3	1600	279.1	—4.8

Table CXVI.—Comparison for Potassium Chloride, Ammonium Chloride.

(Jones and Knight).

	KCl		NH$_4$Cl			KCl + NH$_4$Cl	
V.	μ_v 12°.	*V.*	μ_v 12°.	Sum.	*V.*	μ_v 12°.	Difference.
1	81.95	1	81.10	163.1	1	154.9	8.2
2	84.38	2	83.55	167.9	2	161.1	6.8
5	87.82	5	87.66	175.5	5	170.5	5.0
20	92.88	20	93.19	186.1	20	181.3	4.8
100	98.69	100	99.94	198.6	100	194.7	3.9
200	101.3	200	101.3	202.6	200	199.7	2.9
1000	103.3	1000	103.7	207.0	1000	208.7	—1.7

Table CXVII.—Comparison for Potassium Chloride, Ammonium Chloride.

	KCl		NH$_4$Cl			KCl+NH$_4$Cl	
V.	μ_v 0°.	*V.*	μ_v 0°.	Sum.	*V.*	μ_v 0°.	Difference.
1	61.48	1	61.03	122.5	1	121.2	1.3
2	62.97	2	62.51	125.5	2	122.8	2.7
5	65.83	5	63.97	129.8	5	126.9	2.9
20	68.59	20	68.13	136.7	20	133.4	3.3
100	72.13	100	71.64	143.6	100	141.2	2.6
200	73.73	200	72.89	146.6	200	144.9	1.7
1000	74.31	1000	74.10	148.4	1000	147.5	0.9

Table CXVIII.—Comparison of Differences.

V.	Diff. 0°.	Diff. 12°.	Diff. 25°.
1	1.3	8.2	24.1
2	2.7	6.8	18.5
5	2.9	5.0	12.8
20	3.3	4.8	10.4
100	2.6	3.9	5.2
200	1.7	2.9	2.7
1000	0.9	—1.7	—2.5

If this change in the conductivity, when the solutions are mixed, is due only to a suppression of ionization, then we should expect the suppression to be nearly the same at the various temperatures, since the dissociation is very nearly the same at these various temperatures (*vide* Tables CXIX., CXX.).

Table CXIX.—Dissociation of Potassium Chloride.

V.	α 0°.	α 12°.	α 25°.
1	0.827	0.793	0.768
2	0.847	0.817	0.802
5	0.886	0.850	0.831
20	0.923	0.899	0.905
100	0.971	0.955	0.954
200	0.992	0.981	0.970
1000	1.00	1.00	0.993

Table CXX.—Dissociation of Ammonium Chloride.

V.	α 0°.	α 12°.	α 25°.
1	0.824	0.782	0.715
2	0.844	0.806	0.755
5	0.863	0.845	0.805
20	0.919	0.899	0.878
100	0.967	0.964	0.953
200	0.984	0.977	0.970
1000	1.00	1.00	0.997

If the suppression of the ionization is the only cause of the diminution in the conductivity when the solutions are mixed, then the greatest diminution should take place where the more highly dissociated salts are mixed; that is, the diminution in conductivity should be slightly greater at 0° than at 12°, and slightly greater at 12° than at 25°. Just the opposite is shown to be true by Table CXVIII. Again, if this lessening of conductivity is dependent upon the amount of dissociation alone, then, since the difference between the dissociation at 0° and 12° is the same or a little greater than the difference between the dissociation at 12° and 25° (save in some cases in the ammonium chloride), we should expect to find the difference between the columns headed Diff. 12° and Diff. 0°,in Table CXVIII., the same or slightly greater than the difference between the columns headed Diff. 12° and Diff. 25°. The opposite is true—the difference between columns 2 and 3 being from two to four times as great as that between 1 and 2, up to $V = 100$. At $V = 100$ the differences are the same, and at $V = 200$ and $V = 1000$ the columns headed Diff. 25° becomes smaller than the other two.

We must, then, look elsewhere for the cause of at least a part of the change in the conductivities, since it is evidently not due *solely* to change in dissociation, especially since some of the solutions mixed are nearly isohydric. There are three other factors which might come into play: Change in hydration, giving rise to a change in the dimensions of the ionic sphere; change in the viscosity of the solution with change in temperature; change in the number of the dissolved particles (ions and molecules). Of these three possibilities the first probably does not affect the conductivity appreciably, there being little hydration in these cases. The second is probably the principal factor in causing changes in the conductivity with changes in temperature. The third—change in the number of the dissolved particles—may also play some part, since the value of α becomes smaller with rise in temperature, and, other things being equal, the fewer the number of ions and molecules with which a moving ion must collide, the less the friction it will encounter. The differences in the values of columns 1, 2, and 3 are greatest for the most concentrated solutions, and it is in these solutions that the greatest change in the value α, with rise in temperature, is noted.

Clearly, values for α which are based upon the conductivity of the completely dissociated molecules at high dilution cannot be correct, since the conductivity of this completely dissociated solution must be considerably altered by change in viscosity and in the number of dissolved ions or molecules, both of which factors enter on increasing the concentration, the number of ions and molecules present undergoing especially great alteration.

SUMMARY.

It has been shown:

1. That the complexity of the hydrates formed by a salt is a function of the amount of water present as solvent.

2. That when two salts are present in the same solution, the complexity of the hydrates is somewhat less than in separate solutions of these salts, each salt tending to dehydrate the other.

3. That the ions and the molecules of salts probably have different hydrating power.

4. That the hydrating power of the molecules is in some cases probably greater than that of the ions into which these molecules dissociate.

5. Additional proof is furnished for the view that the conductivity method is by no means an accurate measure of dissociation.

6. It has been pointed out that the diminution in conductivity which takes place when two electrolytes of the type potassium chloride, ammonium chloride are mixed is probably not due entirely to suppression of ionization, but also to

A. Change in the viscosity of the solvent;

B. Change in the size of the ionic sphere, due to alteration in the amount of water which the ion must drag with it through the solution.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1907.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STUDIES IN CATALYSIS.

III. THE THEORIES OF ESTERIFICATION AND SAPONIFICATION.

BY JULIUS STIEGLITZ.

I. In Reply to S. F. Acree.

As I am compelled to reiterate all the main points of my article in the December number of THIS JOURNAL[1] on Mr. Acree's work,[2] and so much the more insistently as he himself has furnished conclusive proof of the justice of my claim in his recent article,[3] I wish to precede my discussion with an expression of regret that in a minor respect my statement that there were no new principles at all in his September article unconsciously was made too sweeping: I find that I overlooked his conclusion that a positive acceleration by acids may be the result of the decomposition of a nonionized salt and not the result of the greater ionization of a salt *versus* a weak base —the latter being the *most common* and most *important* cases of acid catalysis and the only ones we investigated.[1] Acree's conclusion is a welcome addition to the theory and I regret that I overlooked it in the first reading of his long paper—more important points in it demanding my chief attention.

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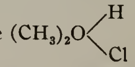
[1] **38**, 743.

[2] THIS JOURNAL, 38, 258.

[3] *Ibid.*, **39**, 145 (1908).

(1) Turning now to his defense, his first and main line of defense is the "tu quoque," a plea made so wildly[2] in this case that Mr. Acree undoubtedly overlooked the fact that, when made, it must always involve, *eo ipso*, a confession on the part of him who uses it. To substantiate his peculiar defense, he seems anxious to discover who discovered my theory of esterification and saponification for me—it happens to be the one that seems to be right.[3] To that purpose he first feels impelled to proclaim Kastle as the original discoverer of the theory of oxonium salts[4]—salt and ion being, it appears, *one* of the strategic points in this controversy; Collie and Tickle and v. Baeyer, to whom I[5] and every one else had given credit for the discovery, must step down and give way to a chemist who discovered that hypothetical "addition products" of acids with the oxygen of esters and similar bodies (making the oxygen quadrivalent) were *salts* without once calling or pronouncing them salts[6]; the five times he speaks of them it is as "addition products," a noncommittal term used by chemists since Friedel, in 1875, discovered methyl ether hydrochloride, also assumed that it could have the structure  $(CH_3)_2O\langle^{H}_{Cl}$,

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[1] In THIS JOURNAL, **31**, 458 (1904) we described, however, a case of anticatalysis (retardation) due to salt formation.

[2] See the constant reiteration, *Loc. cit.*, pp. 146_4, 146_{-1}, 148_1, 148_7, 149_{23}, 150_3, etc., and finally p. 156_1; (the sub-indices indicate the numbers of the lines).

[3] Report of the Congress of Science and Arts, IV., 276 (1904). Goldschmidt has since published similar independent conclusions, which is very gratifying. They are in one minor but very interesting point different from mine. This will be discussed in a later paper.

[4] *Loc. cit.*, pp. 147, 149, etc., 156.

[5] Credit was given by me to v. Baeyer for the discovery that esters form oxonium salts. St. Louis address, *loc. cit.*, p. 281 (1904). THIS JOURNAL, **39**, 48 (1908). Cf. Acree: *Loc. cit.*, p. 156.

[6] *Vide* Kastle's own summary, P. Am. Ass. Adv. Sc., **47**, 238.

compared it with a sulphonium salt to justify the *quadrivalence* of the oxygen, and still did not consider it a salt;[1] Kastle[2] wrote strictly in terms of the ionic theory, calling an ion an ion, an acid an acid, a salt a salt every time he meant to do so, but for the oxygen compounds he always used the longer noncommittal term "addition product"—simply, I presume, because he had no evidence that they were salts and, as an honest chemist, did not choose to call them salts. But Mr. Acree takes it upon himself to introduce into a printed quotation from Kastle the words (Kastle's salt) without a word of comment or explanation[3] to his readers, and ever thereafter it is "Kastle's salt," with priority over Collie and Tickle and v. Baeyer in the theory of oxonium salts and over Stieglitz in his theory of esterification.[4] I only dwell on this matter to show what means were employed to bolster up that "tu quoque."

(2) Even more apocryphal is Mr. Acree's claim that "although, then, Kastle and Frazer had, in 1898, advanced *the vital points* of Stieglitz's paper, Stieglitz did not acknowledge their priority in the matter"[5] and his claim that Bredig's work on the catalysis of hydrogen peroxide is as "good evidence of the correctness of the views of Kastle, Euler, Acree, Bredig, Lapworth, Stieglitz, and Goldschmidt on the hydrolysis of esters, as was Mr. Stieglitz's work on imidoesters."[6] Strange, for the views of Kastle, Acree, Euler, and Lapworth are absolutely at variance with the facts of experience[7]—for instance, with that trifle called the law of mass action—and they are so just because their fundamental assumptions or "views" are *wrong*. In particular, Kastle and Frazer's theory leads to the astounding conclusion that the addition of a

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[1] Bull. Soc. Chim., **24**, 261 (1875). See the original for the old-fashioned terms used.

[2] *Loc. cit.*

[3] The words are bracketted by Acree, as if they occurred in another part of Kastle's text (*loc. cit.*). If they occur in the *written* manuscript readers should have been so informed and told that in Kastle's own abstract of his own paper such an assumption was *suppressed* under a noncommittal term. I would say here that *I hold Kastle and Frazer absolutely innocent in the extraordinary use that has been made of their work.*

[4] The salt idea alone, as will appear presently, wrongly used, leads to absurd conclusions.

[5] *Loc. cit.*, p. 148. Italics in the original.

[6] *Loc. cit.*, p. 150.

[7] See the discussion of Bredig's work below, on p. 425.

catalyzing acid must retard esterification and saponification! My theory, Acree admits, does accord with the facts of experience. How is it possible, then, that its *vital points* were contained in the theories of these men and especially in that astonishing theory of Kastle? As a matter of fact, Mr. Kastle's *fundamental assumption* that the saponification of esters, amides, etc., is essentially the same in kind as the hydrolysis of metal salts[1] is an absolutely wrong and fatal one; a very similar assumption is the fatal assumption on which my own first crude views[2] on saponification and esterification—published in THIS JOURNAL two years before Kastle's—went to pieces; it is the fatal assumption in Euler's theory;[3] and also, from what I can make out of the printed record in Mr. Acree's views of 1902,[4] which are essentially similar to those of Euler's (1901), it is an assumption which inevitably leads to the *reductio ad absurdum*, with the aid of the law of mass action,[5] that acids must either retard esterification and saponification or not affect them at all, whereas, we all know, they just happen to accelerate both. And the fact that Acree does not recognize this even now, that he claims that Kastle's theory contained the "*vital points*" of my own, proves conclusively, it seems to me, that in his own work he has used my theory and conclusions blindly, appreciating the results as concordant with the facts, overlooking, it seems, its very essence.[6]

(3) Again, feeling the weakness of his position, he seems to find the literature on his own views mortifyingly silent and even contradictory on this point of salt formation, the single point he can see in this whole matter, and so he seems at great pains to dress it up a bit in the light of new discoveries.

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[1] I have given the sense correctly, the sentence is inverted to meet grammatical requirements. Cf. Acree: *Loc. cit.*, p. 147.

[2] Lengfeld and Stieglitz: THIS JOURNAL, **16**, 77 (1894). Stieglitz: *Ibid.*, **21**, 101 (1899). See details below, on p. 422.

[3] Wegscheider: Z. physik. Chem., **39**, 257 (1901).

[4] See below, p. 406. Mr. Acree (1902), *exactly like Euler* (1901), represents an *ester* (*e.g.*, enz. $C_6H_{11}O_5$ Ac), as *ionizing* into an *alkyl ion* (enz. $C_6H_{11}O_5$) and an *acid ion* (Ac) (See the sign of reversal in line 21, page 406 below) and as being hydrolized by the *direct union* of the hydroxyl and hydrogen ions of water with the above ions. The fallacy involved in such assumptions, demanding a retardation where an acceleration occurs, is exposed in detail below on p. 406.

[5] Page 417.

[6] See the analysis of my theory, p. 416.

In 1902,[1] speaking rigorously *in terms of the ionic theory*, he wrote of "double compounds" of enzyme and glucose, and of enzyme and glucose ester, using the word "double compound" the three times he speaks of them; but in 1908 these "double compounds" are transformed by a *tour de force* into *salts*!

Mr. Acree (1902):[1] "Nasse's hypothesis might be restated as follows: Glucose gives no hydroxyl ions, and hence dilute acetic acid does not act upon it. Supposing that pancreatin has the power to unite with glucose and that in this double compound the hydroxyl groups of the glucose become hydroxyl ions; then the ionized acetic acid can act upon this double compound, forming water and the double compound, enzyme-acetylglucose, which may break up into the enzyme and acetylglucose. The enzyme which is thus regenerated may then act upon another molecule of glucose (or the acetylglucose), causing other hydroxyl groups to be changed to hydroxyl ions, and hence the process is repeated.... ..." "The entire action can be represented as follows:

$$
\begin{aligned}
&C_6H_{11}O_5OH + HAc + \text{enz.} \rightleftharpoons \\
&\quad \text{enz. } C_6H_{11}O_5(OH) + H + Ac \rightleftharpoons \\
&\qquad \text{enz. } C_6H_{11}O_5 + OH + H + Ac \rightleftharpoons \\
&\qquad\qquad \text{enz. } C_6H_{11}O_5Ac + H_2O \rightleftharpoons \\
&\qquad\qquad\quad C_6H_{11}O_5Ac + \text{enz.} + H_2O.\text{"}
\end{aligned}
$$

Mr. Acree (1908):[2] "Our idea that *catalyzers accelerate such reactions through double compound or salt formation*[3] was expressed by the sentence (p. 372): 'Hence we are very sure that if any changes take place according to the above equation, *the enzyme must take part in the reaction or act as a catalytic agent*,' and by the definite use (p. 372) of *enz.* $C_6H_{11}O_5Ac$ (enzyme-ester *salt*!)[4] and *enz.* $C_6H_{11}O_5OH$ (enzyme-glucose *salt*!)[4] in our equations."

Why was this effort made to force the term *salt* in this sense into his views against the printed evidence? There was merit in the original idea (Nasse's or Acree's?) that an enzyme might in a physical way *cause glucose to ionize as a base*, much as water ionizes sodium hydroxide; *but what can salt formation have to do with that*? Does water form a *salt* with sodium hydroxide when it ionizes it? Does it form a salt with sodium chloride in causing it to ionize? The term "salt" is a commonplace technical term, which we use when we mean to use it, and for which the term "double compound" is never used as a substitute. Does Mr. Acree suppose that any court would for one moment uphold his contention with such printed evidence and facts before it? As a matter of history, there is no connection whatever between Acree's work of 1902, when he considered, as did Euler, that esterification and saponification result from the direct union of ions (purely ionic reactions), and Acree's work of 1907, which, in method, material, principles, attitude, and conclusions, bears a most striking resemblance to my own. The meaning of that effort to connect his work of 1907 with that of 1902 by calling double compounds *salts* must be obvious to every one.[1]

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[1] This Journal, **28**, 372. All chemists interested are earnestly requested to read in the original the page referred to by Mr. Acree, in fairness to him. I have read it *ten times* and cannot read it in any other light than that presented in the text.

[2] *Loc. cit.*, p. 148.

[3] Italics in original.

[4] Italics mine.

(4) Mr. Acree charges that Kastle, Euler, Acree, Bredig, and Lapworth had made all of my fundamental assumptions; I have already pointed out that the assumptions of Kastle, Acree, Euler, and Lapworth[2] were wrong and could not very well have been the ones that led me to a correct theory. But Mr. Acree entirely overlooked the greatest difference in our work, *viz.*, that I approached the subject of esterification and saponification by the path of *experimentation* with the imidoesters and arrived at last, after many a wrong turn,[3] only through the teachings of experimentation and the application of the laws of mass action and dynamics, at what appears to be the truth. But to do so I had to make the most radical assumption[4] of all, which he overlooks deliberately or by a most unfortunate fatality. I had to assume at the very outset

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[1] One will also look in vain for any justification for Acree's claim (*loc cit.*, p. 149) that he had in 1902 the "idea that the basic and acid groups of the enzymes cause salt formation and decomposition "

[2] See below, p. 425, in regard to Bredig's suggestion.

[3] This Journal, **16**, 77 (1899); **21**, 106 (1899).

[4] This assumption has been more than justified and confirmed by our results, I believe.

that the canons of the current definitions of catalysis as general ones were artificial, masking the very facts we were trying to get at;[1] and discarding these artificial so-called "laws of catalysis," I tried to take a new start on a rational basis so as to study the action freely by measurement of the factors involved,[1] formulating the result in terms of the law of mass action. This is for me one of the most important points in the whole controversy. My December article was written largely for its sake, although I have shown that I have other serious ground for complaint against Mr. Acree.

Mr. Acree obviously has missed, by chance or knowingly, the whole point of my work. He says (p. 153): "I believe that if Mr. S. had at that time really had the very important idea that the second and third laws do not always hold, he would have been as eager then as he is now to get credit for the fact and would have said something about it in his St. Louis address." As a matter of fact, I considered them of so little importance then (and do so now) that I cast them aside as worthless and artificial in the very opening of that address. Can one do more?

Besides overlooking the fact that I did abandon these principles, a fact obvious to every man of even an average intelligence who can read English, Mr. Acree, by *wrong quotations*[2] of my articles, makes me say in the matter the exact opposite of what I actually wrote. Would an innocent man stoop to such practices? I have room only for three quotations:

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[1] St. Louis address, *loc. cit.*, p. 278.

[2] His quotations *loc. cit.*, pp. 153–4) are as misleading as can well be found in any literature, scientific or current. Readers interested are requested to read the original article and compare its whole tenor with the way he has presented it, if they believe I have characterized his method too severely. The limitations of space make only one quotation from the group possible (the third in the text).

(*a*) My original statement:[1] "In that address, the first vital and decisive step was taken to depart from the old idea, that catalytic action can be studied only in reactions which complied with the three fundamental principles so long held regarding catalysis, *viz.*, that the acceleration is proportional to the concentration of the catalytic agent, that, in particular, the catalytic agent must appear to act by its presence simply, and not to form a compound in quantity with any of the components, and finally that the condition of equilibrium in a reversible reaction must not be measurably changed by the presence of a catalytic agent."[2]	Mr. Acree's version (claiming to give my fundamental principles; *vide* the original, This Journal, 39, 146, for the exact phraseology): "Mr. Stieglitz says (page 744): 'In that address, the first vital and decisive step was taken to depart from the old idea that .... the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components.'........"
(*b*) My original statement:[3] "Taking the question of *acceleration* alone in a positive or negative direction, as *the keynote of all catalytic action* ...."[4]	Mr. Acree's version:[5] "Stieglitz's KEYNOTE, ACCELERATION THROUGH SALT AND ION FORMATION...."[6]

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[1] This Journal, **38**, 744.

[2] The rather radical nature of the step is clearly seen from a statement in Mellor's "Chemical Statics and Dynamics," p. 252, according to which a change in equilibrium might be employed in doubtful cases as *a test for catalytic actions*. "If a substance changes the velocity of the reaction and, at the same time, has no influence on the equilibrium constant, we are dealing with catalysis pure and simple."

[3] *Loc. cit.*, p. 744. Italics as in the original.

[4] See , Part III p. 426.

[5] *Loc. cit.*, p. 146.

[6] *Loc. cit.*, p. 744. I only emphasized then, as I do now, *our experimental proof* of the connection between salt and ion formation and accelerations produced by the catalyzing acid.

(*c*) And this, the worst of all, where, discussing my attitude in the crucial question, he commits me to the exact opposite of what I wrote. My original statement:[1] "The simple application of our common laws of equilibrium to the proved fundamental idea led, mathematically and chemically, directly to the three principles mentioned above *in the case of very weak bases*, like methyl acetate, *when the amount of salt formation lies beyond the scope of our methods of experimental measurement.* For all other cases the three fundamental principles consequently do not apply and in *no* case do they apply rigorously."

Mr. Acree,[2] quoting me, stops point-blank with a period, in the middle of a sentence, leaving out the whole italicized and therefore emphasized part of the original, without a word of explanation, and italicizes[3] a *different phrase*: "Mr. Stieglitz states, in discussing the catalysis of esters, that (p. 745) 'the simple application of our common laws of equilibrium to the proved fundamental idea of salt formation led, mathematically and chemically, *directly to the three principles mentioned above.*' "

He never once squarely faces the *fact* that the three principles were abandoned as an obvious necessity, *ab initio*, and that all of our results for five years have been obtained with regard to only one law, the law of mass action[4], with utter disregard and largely in contradiction of the principles.

(5) The result of this method of approach is a formulation consistent with all the facts. Mr. Acree followed a similar method—only he started with the machine *turned upside down.* Using reactions, in his first proof,[5] which violate the definitions[6] of catalytic actions, on which alone the so-called laws of catalysis are based and to which alone they are said to apply, he finds of course that they do not hold (no one ever claimed they

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[1] *Loc. cit.*, p. 745. Italics as in the original.

[2] *Loc. cit.*, p. 153.

[3] He acknowledges the italics, without further explanation.

[4] St. Louis address, *loc. cit.*; THIS JOURNAL, **39**, **29**; and eight long papers, the condensed result of which were presented at Baltimore in April, 1907.

[5] *Loc. cit.*, pp. 348–352.

[6] Nernst: "Theoretical Chemistry," p. 566. Ostwald. Z. Elek. Chem., **7**, 995 (1901), and Z. physik. Chem., **36**, 643. Mellor: *Loc. cit.*, p. 246, 250, etc. *Vide* Acree himself: *Loc. cit.*, 259, 348.

should) and announces his discovery, *e. g.*, the change of equilibrium with the oximes.

The catalyzing acid enters into the end products, forming hydroxylamine hydrochloride and hydroxylamine ions, and some acetoxime hydrochloride and its ions, and the action thus violates the clause in the definition from which the "law" concerning equilibrium is deduced.[1] He might have saved himself the trip around the circle, any investigator in the field might have told him that. A chemist who decides to apply the term "catalytic" to actions lying outside of the definition[2] *eo ipso* leaves the "laws" behind,[3] because they are based, *e. g.*, by thermodynamical reasoning, on the definition itself![4] It is altogether a different matter to prove, as I believe I did, that there is *no essential difference in the fundamental dynamic equations*,[5] *in the fundamental mechanism, mode, and causes of catalysis*[6] (acceleration, new definition[7]) for reactions, on the one hand, which lie outside of the old definition (catalysis of imidoesters and similar bodies) and for which the principles cannot and do not hold,[1] and for reactions, on the other hand, like esterification and saponification, which lie within the old rigorous definition and for which the laws *incidentally*[2] hold, and to claim that it consequently is not logical to distinguish one class from the other. Mr. Acree has asked me for my experimental proof;[3] our whole work, experimental and theoretical, proves, I believe, and was in a large measure designed to prove, the relations between the two types of catalytic action, those for which the laws cannot hold and those for which they hold incidentally, as has just been made clear. Having reduced the whole matter on the basis of our *experimental work* with the imidoesters[4] to the mathematical terms of the law of mass action, we have not felt it necessary to confirm this old law and its consequences all over again;[5] but if Mr. Acree is anxious to collect circle proofs, he can make all the circles he chooses around experiments by McCracken, Derby, Schlesinger, and Miss Barnard; we have assumed the law of mass action to be true, even when it conflicted with the "principles," and have calculated our results accordingly.

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[1] Ostwald's definition (*loc. cit.*) is: A catalytic agent is every substance that changes the velocity of a chemical reaction, *without appearing in its end products.* All of Acree's illustrations, given in the first proof, violate this italicized part of his definition. Even if we extend the definition to include so-called autocatalytic actions *the law about equilibrium, etc., is based rigorously on the premise that the catalyzer does not enter into the end products. Vide* Nernst: *Loc. cit.*, p. 566; van't Hoff: "Lectures on Physical Chemistry," I., 214; Bredig: "Ergebnisse der Physiologie," (1902) 172; Mellor: *Loc. cit.*, etc.

[2] For instance, if we *call* the saponification of an ester by an alkali a catalytic action, it is obvious to every one, without experimentation, that the catalyzer used in different proportions must change the apparent equilibrium between ester, water, acid, and alcohol, because it enters into the products of the reaction. This is a rather rough but pertinent parallel to Acree's oxime proof; there he had a weak and a very much stronger base on the two sides of the equation, here we have a very weak acid, ($CH_3C(OH)_2OR$), since $CH_3C(ONa)(OH)(OR)$ is generally considered to be an intermediate product, and a much stronger acid, acetic acid, on the two sides of the equation. It is a fact significant of the *artificialness* of the whole modern treatment of the subject that this important reaction, in its general characteristics really typically "catalytic," is *seldom* spoken of in text-books and in discussions under "catalysis." When the catalytic action of hydroxyl ions is referred to, the instances most often cited are the far less important ones of the change of hyoscyamine into atropine, the change of acetone into acetonyl acetone, etc., actions which happen to conform to the narrow definition and its principles for the reasons given by me, THIS JOURNAL, **38**, 745, for the esters, etc.

[3] That is why I discarded them *ab initio*, *loc. cit.*

[4] *Vide* also Stieglitz: THIS JOURNAL, **39**, p. 56, line 30.

[5] St. Louis address, *loc. cit.*, and THIS JOURNAL, **39**, p. 57, first three lines.

[6] THIS JOURNAL, **39**, 56, 57, 63, etc.

[7] St. Louis address, *loc. cit.*, and all my articles.

In a word, Acree,[6] using, to a large extent, the same type of compounds as I did, has come through an *illogical, unscientific circle* in 1907 to the point I started from in 1904. Putting the cart before the horse, to use a homely parallel, does not change that fact. I would assume, too, that he did not understand the significance of my stand and my mathematical presentation, if he did not seem to show, by his misquotations, that he knows very well what he is about.[1]

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[1] St. Louis address, *loc. cit.*, p. 279, fourth equation; and THIS JOURNAL, 39, 35, equation (6), etc.

[2] St. Louis address, p. 278, line 9, and p. 280.

[3] *Loc. cit.*, pp. 152–3.

[4] It was necessary to prove *experimentally* that the positive ion of the imidoesters, as determined by the *hydrolysis equation* (6) and by conductivity and velocity measurements, is the *reacting component.*

[5] THIS JOURNAL, **39**, p. 57. Mr. Acree need not trouble himself to make any laborious calculations with the fundamental hydrolysis equation (6), which causes the divergence from the laws: he will find in my paper on the velocities of the molecular rearrangements of aminophenylalkyl carbonates (*loc. cit.*) many instructive illustrations of the wide divergence from even a proximate proportionality between salt and acid in hydrolyzed solutions of salts of weak bases with strong acids; *e. g.*, in Table III. (p. 475) the proportion of salt to total acid varies from 59 to 82 per cent, according to the dilution used, and in Table IV. the salt $[(1-pt_t)]$ varies from 82 to 12 per cent, according to the amount of acid present.

[6] His "second proof" (*loc. cit.*, pp. 349 and 352) stands on the old as well as the new definitions of catalytic action and is a very pretty one: only on account of its intimate association on p. 349 with his first proof, in which he takes my ground, in however an unscientific way, and without acknowledgment, no special reference to it was made by me in my December article.

(6) In closing this introductory statement, I should like to ask Mr. Acree to answer, to his own satisfaction, at least, the following plain questions: Why he felt impelled to rush off into a "tu quoque" defense, implicitly a confession? Why he felt it necessary to challenge Collie and Tickle's and v. Baeyer's rights to the discovery of the oxonium salts by speaking of "Kastle's salt" against the *printed evidence* in the case? How Kastle's theory, whose fundamental assumption is altogether wrong, can possibly contain the *vital points* of my theory, whose fundamental assumptions seem to be right? Why he felt it necessary to try to connect the Acree of 1907, standing altogether on the same ground as myself, using and discussing reactions with acids, bases, and salts to a very large extent very much like my own, with interpretations in almost all cases absolutely like my own (as presented in the Baltimore address), *minor* variations *ad casum* being allowed for—why he felt it necessary to connect this Acree of 1907 with the Acree of 1902, who had stood on Euler's impossible grounds, by writing now of a *salt* combination of the enzyme against all the *printed evidence* in the case? Why he felt it necessary to write now about a "mutual benefit" arrangement to correct some alleged "wrong ideas" of mine about phenolphthalein—wrong ideas which existed only in his own vivid imagination—as representing the subject of the conversation in which we spoke only of my methods and my work in the summer of 1905? (See the *printed evidence* in Part IV. of this article.) Whether the ideas of Kastle, Euler, Lapworth, and Acree, leading to the conclusion which is the reverse of the truth, that acids would either retard or

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[1] I have, of course, never had the slightest objections to Mr. Acree working in the same field and by the same methods as myself; the more the better. I have always encouraged him in his work when opportunity offered and he had privately recognized my priority by giving me first choice in a friendly division of the field; it was only to protect my priority also in public that I was compelled to enter my protest in December. I wrote him in October that two lines of acknowledgment in his introductory statement would have been quite enough.

not change at all the speeds of esterification and saponification, would not discourage any investigator from following their footsteps into the paths of error, ridicule, and idle speculations at variance with the fundamental law of mass action? Whether it is not true that in this hopeless waste of hopeless hypotheses only experimental facts and their mathematical formulation[1] could have led me and did lead me to the truth and the new ideas underlying it by the easiest of all paths, the path of the palpable fact—just as Collie and Tickle could not help recognizing oxonium salts when they had them in their very hands? Whether, according to all the *printed evidence*, in order to get into my path of experimentation, in order to "measure all essential factors," I did not find it necessary to discard and did discard, as general principles, *ab initio*, all the artificial canons and laws of catalysis which stood in my way, and took a new start? Whether our investigations, coming out in ten articles, were not started, carried out, and reported, irrespective of the fact whether they complied with these canons or not (and most often they do not), as long as they complied with the laws of dynamics and our conceptions of catalysis? And most emphatically—why he felt impelled to deny and misrepresent my stand on this question *by wrong quotations of printed evidence*?

And, finally, I must ask Mr. Acree whether it is not true that both the printed text and the equations in his 1902 article represent the esterification of glucose to glucose acetate as resulting from the ionization of glucose as a carbonium alcohol base, an ionization supposed to be facilitated by the enzyme, and of acetic acid as an acid, and as being due to the direct union of these ions to form the ester as a purely ionic reaction, very much in the same way as presented by Euler in 1901? Whether such views are not at variance with all the facts known about ionic reactions, at variance with the facts of organic chemistry, at variance with the law of mass action, and absolutely different from the views of Bredig, Stieglitz, and Goldschmidt? And, such being the case, why he presents these wrong views of 1902 now in 1908 as correct, as being as correct as the views of Bredig, Stieglitz, and Goldschmidt?[1] And, lastly, whether it does not *sometimes happen* that when a man rushes into print with only half-assimilated ideas, he is liable to reproduce these ideas upside down, in an altogether illogical and unscientific manner?

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[1] See the laborious formulae and calculations, THIS JOURNAL, 39, pp. 35–41.

II. The Theories of Esterification and Saponification.[2]

It was the plan to include in my first article the usual part[3] treating critically of all previous attempts, miscarriages though they were, which could be remotely connected with the ideas laid down in these papers. When, for reasons best known to Mr. Acree, it became necessary to send in my article at once, in part, lack of time to carry out this not very profitable work led me to omit it.[4] I am sure the readers of this paper will admit that no injury was thereby done to anybody, feelings have been rather spared than hurt, and in fairness to all I did not refer to my own first views,[5] published two years before Kastle's, in some particulars very similar to them and certainly just as wrong. I will take this opportunity of adding the omitted part and discussing, somewhat more critically than Mr. Acree chose to do in his last article, the relations between the various theories.

(1) *The Writer's Theory (1904 and 1907).*—I have never claimed that I was the inventor of the principle that catalytic action is due to the formation of salts and their ionization, a principle which was most clearly and emphatically enunciated by Euler in 1901 as a hypothesis, without rigorous experimental proof, although with very good arguments.

But, I believe, we got the first *experimental* proof of the influence of salt formation and ionization in this class of reactions, and have followed the guiding knowledge of this proved *fact*,[1] not of the hypothesis and its futile application to the theory of esterification,[2] ever since. The theory of ionization is an admirable one; it has done great service to chemistry and I am and have been an ardent adherent of it—but ionization is not the whole of chemistry: applied by physical chemists indiscriminately to organic reactions without due regard to the facts of organic chemistry,[3] it often leads to wrong conclusions,[4] and applied by organic chemists to organic reactions without due respect for the laws of physical chemistry, it sometimes leads to monstrous theories of catalysis.[5] The idea of ionization as a cause of catalysis, applied by itself in a purely hypothetical way by Euler, and later much in the same way by Acree,[6] to esterification and saponification, led to a theory in which these are represented as purely ionic reactions; its conclusions are so much at variance with facts, with the results of experience, and with the law of mass action, that such a theory of esterification appears altogether untenable.[7]

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[1] *Loc. cit.*, p. 150, last paragraph.

[2] They are considered up to 1904, the date my theory was published.

[3] The long reference to *Euler's* work, THIS JOURNAL, **39**, 62 (Article 1), was hastily added as the "rudiment" of such a chapter, as Euler, in spite of the radical faults in the application of his own theory, which made it appear useless (Wegscheider. *Loc. cit.*) unquestionably was the first champion of ionization as a cause of catalysis, *e. g.*, in esterification and saponification.

[4] Then, Mr. Acree had been using Kastle, Acree, Euler, etc., as a pretext for ignoring my protests and I wished to see him committed in print to this defense before writing this chapter.

[5] Lengfeld and Stieglitz: THIS JOURNAL, **16**, 77 (1894). Stieglitz *Ibid.*, **21**, 101 (1899). Dr. Lengfeld will confirm my statement that I was chiefly responsible for that part of our paper and *for all the mistakes it included.*

Work with the imidoesters led me, by experiment and calculation, to the conclusion that the positive imidoester ion is the reacting component[8] when the esters are decomposed by water in the presence of acids, and the result was formulated mathematically on the basis of the law of mass action.[9] This *experimental*[10] result and formulation were extended to the consideration of esterification and saponification and a theory was developed that was consistent at the same time with the fact[1] we had ourselves discovered, *viz.*, that the positive ester ion is the reacting component in a strictly analogous reaction;[1] consistent also with v. Baeyer's proof that the esters form oxonium salts,[1] with Coehn's proof that oxonium salts are true electrolytes,[1] with Rosenheim's and Euler's evidence in favor of basic properties of acetic acid;[1] consistent with the long established facts concerning velocities and equilibrium in these interesting catalyses;[1] and consistent above all with the fundamental laws of mass action and dynamics.[1] Credit was explicitly given in the first and all the papers to all these chemists whose results were used.[2]

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[1] St. Louis address, *loc. cit.*, page 281, line 20; THIS JOURNAL, **38**, 744, last lines; and in many other places.

[2] Euler: *Loc. cit.*

[3] *Vide* "Theories of Indicators," J. Am. Chem. Soc., **25**, 1112.

[4] Euler's theories of esterification and saponification are referred to.

[5] I refer to the first theory of Stieglitz and Lengfeld (1894–9), and also to Kastle's, Acree's, and Lapworth's theories, and I characterize them so because theories that attempt to *explain acceleration* in a way that shows there must be a *retardation* or, at best, a *standstill*, are preposterous.

[6] The paper of 1902. He stands on altogether different grounds in 1907.

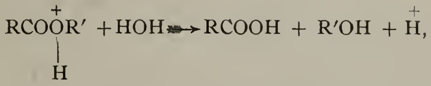
[7] Wegscheider: Z. physik. Chem., **39**, 257 (1901). Acree: THIS JOURNAL, **38**, 343.

[8] It was later found to be the reacting component also in amidine and guanidine formations.

[9] St. Louis address, *loc. cit.*

[10] *Ibid.*, p. 281, line 20.

The fact was therefore clearly recognized that in the catalysis *only the positive ion*, say of the ester, *reacts with water, that it reacts with* BOTH THE COMPONENTS OF WATER, ITS HYDROGEN AND ITS HYDROXYL IONS,[3]



$$\mathrm{RCO}\underset{\underset{\displaystyle \mathrm{H}}{|}}{\overset{+}{\mathrm{O}}}\mathrm{R'} + \mathrm{HOH} \rightarrow \mathrm{RCOOH} + \mathrm{R'OH} + \overset{+}{\mathrm{H}},$$

a result which is not in the least analogous to the hydrolysis of a salt by water, for *in such salt hydrolyses the positive ion reacts only with the hydroxyl ion of water.* That, in a nutshell, expresses the fatal defect in all "hydrolysis of salts" theories of catalysis.

The following condensed mathematical formulation for the simplest cases shows the significance of the newly discovered fact: for the action of water, *with both its ions*, on the positive ester ion, we have the isothermal equation:

$$\frac{dx}{dt} = K \times C_{Pos.\ Est.\ Ion} \times [C_H \times C_{OH}]$$

$$= K \times k \times C_{Ester} \times C_{H^*} \times [C_H \times C_{OH}],$$[4]

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[1] St. Louis address, *loc. cit.*, p. 281, line 20.

[2] Also to Euler's views on catalysis, pp. 277, 280, and repeatedly in our later articles. Reference to Kastle's work (if I had known it), Acree's, and Lapworth's could only have been made in the form of warnings against erroneous assumptions.

[3] *Loc. cit*

[4] For *very weak* bases, we may put $C_{Pos.\ Ion} = k \times C_{Ester} \times C_H$.

in which we recognize the significant accelerating factor $C_H{}^*$. In the hydrolysis of a salt the positive ion reacts only with the hydroxyl ion of water to give the base and we have:[1]

$$\frac{dx}{dt}=K\times C_{Pos.\ Ion}\times C_{OH}=K\times k\times C_{Ester}\times [C_H\times C_{OH}],$$

in which the absence of the significant accelerating factor $C_H{}^*$ is very striking. It is on this account that all theories comparing the hydrolysis of esters with the hydrolysis of salts fail altogether to show any cause for acceleration by the catalyzing acid, the significant accelerating factor $C_H{}^*$ slips from our grasp, with the result, of course, of a *reductio ad absurdum* for the unfortunate theory, which is trying to explain *the very fact of acceleration*. As long as that line was followed, the quest for the truth was hopeless, it seems to me.

Our results were also combined with, and found to be in harmony with, other well-known ideas and facts of organic chemistry, such as the fact that carbonyl (C : O) and carbimide (C: NR) groups are unsaturated,[2] and in particular with the important fact that the decompositions[2] and molecular rearrangements[3] of organic molecules usually, almost always, are slow processes[4] and therefore not the result altogether of purely ionic reactions. And finally, the theory having been established, an attempt was again made to formulate in a preliminary way a reason *why* the *ion* should play such an important rôle, why an acid by forming a positive *ion* should accelerate an action, and it has been pointed out that in all of our experiments a general tendency is exhibited for the positive ion of a weaker base to go over into the positive ion of a stronger base (*e. g.*, an imidoester ion into the ammonium ion), suggesting some kind of electric potential or loss of free energy as a "driving force."[5] Such ideas are very commonly

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[1] The same result is obtained, of course, from

$$\frac{dx}{dt}=K_v\times C_{Base}=K_v\times k\times C_{Ester}\times [C_H\times C_{OH}],$$

as shown below in discussing Kastle's theory.

[2] THIS JOURNAL, **39**, 58. Presented in the Baltimore address.

[3] *Ibid.*, **31**, 458.

[4] See the theory of this in Ostwald's, Bredig's, and Wegscheider's writings.

[5] Credit was given to Euler for a previous formulation of this idea; *vide* THIS JOURNAL, **39**, p. 59.

expressed,[1] and Euler had suggested something of the same kind on the basis of his hypothetical forms of ionization; quite a little experimental proof with actual ions has been brought now in our work. I believe this assumption is the most important element in Euler's work.

There are then in our formulation elements of the theory of ionization, elements, above all, of the laws of dynamics, elements, finally, of a few fundamental facts of organic chemistry. The result is gratifying but in itself nothing to make much of; the theory may not represent a final formulation, but revision will probably be rather in the form of extension than in that of very radical changes of its principles. My own interest in it lies very largely in the experimental method of approach by reactions which do not come under the formal definition of catalytic action, but which, nevertheless, show all its essential features. I trust I may be pardoned for presenting its elements in such detail; it appeared necessary because Mr. Acree, it seems to me, has tried to create the impression that "salt formation and ionization" are about all there is to theories of catalytic action irrespective of the question whether they agree with the law of mass action or not.

Some chemists, we shall now find, had speculated only about the rôle of salt formation and ionization and had developed wrong theories; other chemists had speculated about the rôle of unsaturated valences of carbonyl groups[2] and developed other wrong theories; other chemists had simply taken the mathematical requirements of the law of mass action into account and developed still other wrong theories.[3]

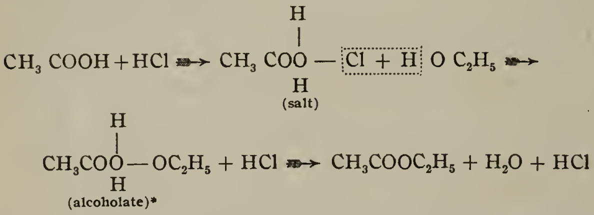
(2) *Kastle's Work* (*1896*).—"On the ethers of carbonic acids, acids act by contact and, without apparently suffering any decomposition themselves, greatly accelerate the action of water on esters; . . ." nothing more definite being in the subsequent phrases. And "in fact no satisfactory explanation of the catalytic action of acids on the ethereal salts of carbonic acids has ever been offered; and until we are

[1] See also Hemptinne and Lowenherz, working under van't Hoff: Z. physik. Chem., **13**, 561 and **15**, 395; and the writings of many other men.

[2] Stieglitz and Lengfeld, Lapworth.

[3] Euler's second theory, discussed below, § 4.

better able to follow the part played by the acid, in its rôle as hydrolyzing agent, speculation as to this difference in their conduct towards the carbonic and sulphonic ethers can be of little, if any, service." This is about all bearing on a theory of catalysis said by Kastle in his own abstract[1] in this Journal of his paper as read before the A. A. A. S. in 1896. It did not sound promising enough to encourage a visit to another library to read the original. But a short time ago, on Mr. Acree's suggestion, I read the original.[2] I have already pointed out that Mr. Acree took it upon himself to insert the words (Kastle's salt) in his quotation of the original, without adequate explanation to his readers. But assuming that Mr. Kastle meant salt and always used only the longer term "addition product" exclusively from conservative, honest habits of mind,[3] I have pointed out that his fundamental assumption, that saponification and esterification are essentially similar to the hydrolysis of salts, is absolutely wrong. If we consider his equation representing the esterification of acetic acid[4]—



$$CH_3\,COOH + HCl \rightarrow \underset{\text{(salt)}}{CH_3\,CO\overset{\substack{H\\|}}{\underset{H}{O}}} — \boxed{Cl + H}\;O\,C_2H_5 \rightarrow$$

$$\underset{\text{(alcoholate)*}}{CH_3CO\overset{\substack{H\\|}}{\underset{H}{O}}} — OC_2H_5 + HCl \rightarrow CH_3COOC_2H_5 + H_2O + HCl$$

we find that the intermediate product marked with an asterisk would obviously represent an *alcoholate* of an oxonium base: this alcoholate could also be obtained directly from the oxonium base, acetic acid, and the weak acid, alcohol: now, any chemist will see that the addition of a strong acid will, by the law of mass action, inevitably reduce the concentration of such an alcoholate,[1] whether we assume the acetic acid to be a very weak or a stronger oxonium base, and reducing the concentration of the acting component, the alcoholate, means that the action will be *retarded—under no circumstances accelerated*—which is in direct contradiction to the facts of observation. The theory of saponification is, if possible, even more astonishing: in the action

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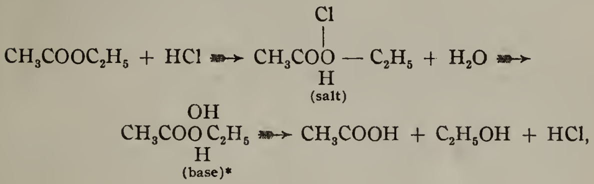
[1] This Journal, **19**, 894. It is all I can find.

[2] *Loc. cit.*

[3] The objections to the theory hold equally whether a salt or an addition product is assumed.

[4] As given by Acree: *Loc. cit.*, p. 147. I have added the names under the formulae to make the text clear.



$$CH_3COOC_2H_5 + HCl \rightarrow CH_3CO\overset{\overset{Cl}{|}}{\underset{\substack{H\\ \text{(salt)}}}{O}} - C_2H_5 + H_2O \rightarrow$$

$$CH_3CO\overset{OH}{\underset{\substack{H\\ \text{(base)*}}}{O}}C_2H_5 \rightarrow CH_3COOH + C_2H_5OH + HCl,$$

the intermediate product marked with an asterisk is a *base*, the oxonium base of acetic ester: to get an acceleration by adding an acid we must make the violent assumption that free bases exist by preference and in greater concentration in acid solutions than in purely aqueous ones.[2] But they just don't, quite the reverse is true, and so here, too, the acid would *retard* saponification. Kastle's theory of saponification would be formulated mathematically as follows:[3]

$$\frac{dx}{dt} = K_v \times C_{Hydroxide} = K_v \times k \times C_{Ester} \times C_{H_2O}.$$

The experimental isothermal equation, whose theoretical significance we developed, is

$$\frac{dx}{dt} = K \times C_{Ester} \times C_{H_2O} \times C_{H}.$$

Kastle's theory, therefore, omits the significant accelerating factor, C_H. Now, this extraordinary theory, which leads to conclusions the reverse of the truth, is flung at the writer in reproach time after time; on page 148 of Acree's outbreak we read: "Although, then, Kastle and Frazer, had, in 1898, advanced *the vital points* of Stieglitz's paper, Stieglitz did not acknowledge their priority in the matter."[1] Does Mr. Acree or any one really believe that a theory so utterly at variance with the facts as is Kastle's, a theory whose main assumption is absolutely wrong, can possibly contain the vital points of my theory, which agrees with the facts? Mr. Acree stands convicted, by this extraordinary summing up of Kastle's theory, of an almost incredible lack of understanding of the simplest foundations of the whole subject or of a deliberate attempt to mislead his readers and to injure the writer.[2]

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[1] A rough but pointed comparison is to compare the relative proportions of sodium alcoholate obtained from sodium hydroxide and alcohol in the absence and in the presence of hydrochloric acid.

[2] *I. e.*, that there is more ammonium hydroxide in a solution of a given amount of ammonia after adding hydrochloric acid than before its addition.

[3] C_{Ester} would be made smaller by the acid, so there would be a retardation.

(*3*) *Lengfeld and Stieglitz's First Work*[3] (*1894*); *Stieglitz's*[3] (*1899*).—If Mr. Acree believes that "views," right or wrong, are all equally good,[4] he should have referred to an article written by Lengfeld and myself in 1894, two years before Kastle's, and still earlier than Acree's, etc. We draw a parallel there between imidoesters and the ordinary esters and compare possible "addition products" of the esters and organic acids with hydrochloric acid,[5] $RC(OH)Cl(OR)$, with the imidoester salts, and show how these intermediate products might be utilized to interpret the reversible reactions of esterification and saponification. For the salts of the imidoesters similar structures $RC(NH_2)Cl(OR)$ are proposed, but their nature as true salts is questioned: in 1899 they were proved to be true salts, but considered to be probably salts of a carbonium type, $R\overset{+}{C}—\overset{-}{Cl}(NH_2)OR$, and as a result of our quantitative work on velocities they were finally accepted as ammonium salts.[6] From this comparison of the organic esters with the imidoesters in 1894 my present theory was evolved slowly, through many errors, from which it was finally extricated by the teachings of rigorous experimental work and calculations on velocities. Of course, no credit at all is claimed for it, so wrong in most of the assumptions—it is much like Kastle's, only he assumes addition products with the oxygen atom, we with the carbonyl group. In this necrology of embryonic, false theories, it has its proper place with its companions in misfortune.

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[1] Italics in the original.

[2] I hold Kastle and Frazer as innocent in the extraordinary use to which their theory has been put.

[3] *Loc. cit.*

[4] *Loc. cit.*, p. 150, last paragraph.

[5] There were undoubtedly numbers of previous writers who assumed similar intermediate addition products. This early comparison with imidoesters is the point I would emphasize.

[6] *Vide* Stieglitz and Barnard: J. Am. Chem. Soc., **27**, 1016, in which v. Baeyer's analogous difficulties with the triphenylmethane bases are discussed.

(4) *Euler's Work.*[1]—This brilliant exponent of ionization as the cause of catalysis applied his theory to esterification and saponification; he assumed forms of ionization of acid esters, etc., that seemed impossible to organic chemists, though they led to what looked to him like promising mathematical equations: but Wegscheider[1] pointed out that his theory did not agree with the demands of the mass action law—a fatal defect, certainly. To overcome Wegscheider's criticism, Euler[2] had recourse to the assumption that the kind of ionization he was thinking of was not *instantaneous*—such a radical assumption, to support other radical assumptions, seems to the writer to be forcing facts to suit a theory and mathematics, instead of working in the approved opposite direction. Besides, they are now unnecessary, as we have satisfactory interpretations without them. In 1904, when my work, as presented at St. Louis, was already complete, Euler brought out a short paper,[3] in which he suggests that the inversion of cane sugar is the result of hydrolysis of a carbonium ion[4] of cane sugar, $C_{12}H_{21}\overset{+}{O}_{10}$, which he assumes to be the active component; again his idea agrees, mathematically formulated, with the dynamic equation for the inversion. But again it must be said that mathematics and the theory of ionization are not all in chemistry. The assumption of a carbonium ion, *i. e.*, of an ionization of cane sugar in one of its alcohol groups according to

$$C_{12}H_{21}O_{10}(OH) \rightleftarrows C_{12}H_{21}\overset{+}{O}_{10} + \overset{-}{OH},$$

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[1] *Loc. cit.*

[2] Z. physik. Chem., **40**, 501.

[3] *Ibid.*, **47**, 355 (1904).

[4] There is a misprint in one of his formulae, but the ionization of the hydrochloride, $C_{12}H_{21}\overset{+}{O}_{10}$ and $\overset{-}{Cl}$, shows unmistakably that he adhered to his old views on this point.

would involve the conclusion that by the addition of, say, acetic acid as a catalyzer, we should get instantaneously the ester, the acetate:

$$C_{12}H_{21}\overset{+}{O}_{10} + \overset{-}{OH} + \overset{+}{H} + CH_3\overset{-}{COO} \rightarrow C_{12}H_{21}O_{10}(C_2H_3O_2) + H_2O.$$

That is at variance with the real facts of the case. If we assume a slow ionization, as above, to prove the correctness of the original assumption, we become involved in an actual self-contradiction. For Euler's mathematical formulation agrees, I believe, with the requirements of the dynamic equation of experience only on the assumption that the reversible reaction of hydrolysis of a salt,

$$K \times Salt = Acid \times Base,$$

adjusts itself at every moment instantaneously—which is a contradiction of the second assumption. And besides, the idea misses the very essence of the cause of the catalysis in the salt formation and ionization of the ester group as a complex ion which reacts with water.

(5) *Acree's Work.*[1]—Mr. Acree's views on esterification and saponification, as expressed in 1902, have already been tpresented above in Part I.[2] It seems to me that hey have the same inherent radical errors in their assumptions as were just now discussed in the case of Euler's theory of esterification and saponification (1901), which Acree's views very closely reflect in all essential particulars. They are, therefore, at variance with the known facts concerning ionic reactions, with the law of mass action, and with the facts of organic chemistry.

(6) *Lapworth's Work.*[3]—Mr. Acree, in the article preceding his controversial one, has already shown that Lapworth's theory is at variance with the requirements of the law of mass action[4] and therefore wrong, as has been shown to be the case

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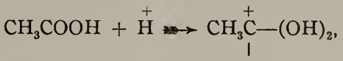
[1] This Journal, **28**, 372 (1902).

[2] P. 406.

[3] Mellor: "Chemical Statics and Dynamics," p. 289 (1904).

[4] This Journal, **38**, p. 342.

for Lengfeld and Stieglitz's first hypothesis[1] and for Kastle's, Acree's, and Euler's theories. I will add this: Lapworth assumes the combination of the hydrogen ion with acetic acid,



$$CH_3COOH + \overset{+}{H} \longrightarrow CH_3\overset{+}{C}—(OH)_2,$$

to be a *slow* process, followed by the more rapid changes of esterification. My theory is based upon the fact of experience that salt formation in homogeneous solution sappears to be an instantaneous process,[2] the action of the alcohol on the complex ion a slow one—the two theories are therefore also in these respects utterly at variance with each other.[3]

(7) *Bredig and Walton's Work.*[4]—The contribution of these chemists to the theory of catalysis of esters consists in the suggestion, made in a footnote in an article on the catalysis of hydrogen peroxide by iodine ions, that the formation of complex ions of esters and cane sugar with hydrogen ions might explain their catalysis. The suggestion is not worked out, no theoretical or experimental evidence brought, and that Bredig himself, at least, did not consider the somewhat strained analogy (see below) to the hydrogen peroxide catalysis as any *proof* of the validity of the hypothesis—as claimed by his newly found and interested champion in Baltimore—is shown by the fact that in his next article on a catalytic action he still refers to it, in only a few casual words, as "nicht unwahrscheinlich"—not improbable.[5] I am very glad, however, to record here the fact that Bredig made a suggestion to the above effect and that it was not referred to before only on account of its being hidden in papers on different topics, which I had no occasion to read. It has no bearing on the

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[1] Lapworth's theory leads to exactly the same intermediate product as we assumed, and with the same fatal result.

[2] THIS JOURNAL, 39, 58. The *decomposition* of the addition product is probably the *slow* process.

[3] Lapworth, *loc. cit.*, also seems to be uncertain about the ionization of alcohol into C_2H_5 and OH ions.

[4] Z. Elek. Chem., 9, 118. I was not acquainted with the original papers until recently my intention was called to them by Acree. In the Centralblatt, 1903 and 1904, in which the two articles are reviewed, there is no word to suggest that any idea as to the catalysis of esters had been advanced.

[5] *Ibid.*, 10, 586 (1904).

development of my own theory, the history of which is on record.

The funniest thing in Mr. Acree's article is the statement (p. 150) that "Bredig's quantitative work on the catalysis of hydrogen peroxide by iodine ions is as good evidence of the correctness of the views of Kastle, Euler, Acree, Bredig, Lapworth, Stieglitz, and Goldschmidt on the hydrolysis of esters, as was Mr. Stieglitz's work on the imidoesters." How one and the same investigation can prove the correctness of the views of five investigators, four[1] of whom have arrived through "their views" at theories at utter variance with the facts of observation, while the fifth arrived at a theory consistent with them, surpasses my understanding. And how an investigation which has only a very superficial resemblance to ester catalysis and, closely considered, very serious differences, can prove a theory of catalysis of esters is also beyond me. Bredig and Walton evidently agree with me on the point of proof.[2] The first reaction assumed in Bredig's work is a *slow* one of *oxidation*:

$$H_2O_2 + \overline{I} \rightarrow H_2O + \overline{IO}.$$

Can this really be considered strictly analogous to the formation of a complex salt and its ions as instantaneous actions in the ester catalysis?

III. The Definition and Theory of Catalysis.

It was and is my intention, when all our articles are published and our experimental material is in print, to submit an article proposing and supporting, on the basis of our results, a broader formulation of the definition and theory of catalysis than is now generally accepted.[3] In the St. Louis address the catalysis of esters—a truly catalytic action, on the basis of current definitions—was connected chemically, theoretically, and mathematically with the decomposition of imidoesters by water and acids, which cannot be considered a catalytic action at all under current definitions. That objection, it may be said, was also raised in 1904 by Professor Walker of Dundee, and conveyed to me through the courtesy of Professor Alex. Smith. From the mathematical formulations[1] it will be seen, however, that *truly catalytic actions* (old style) *must merge by imperceptible degrees into truly noncatalytic actions* (old style), *and that there is no dividing line possible at any point.* Professor Ostwald[2] in another connection, has recognized that such a formulation, *eo ipso,* proves the essential identity of the two extremes.[3] But we were not content with this theoretical closing of the gap between the extremes: our work of the last three years has been largely directed towards closing it by experiment, as far as that is possible, and we believe that we have at last succeeded; the formation of amidines from imidoesters and ammonia is accelerated by the addition of acids and we proved that it is so because minimal but measurable quantities of the positive imidoester ion form the reacting component: on the other extreme, the formation of guanidines from ureaesters and ammonia is also accelerated by the addition of acids, only in this case the catalyzer is almost completely combined with the ureaester and yet the formation of guanidine proceeds according to exactly the same law—based on the law of mass action—as the amidine formation. It may be objected perhaps that neither is, rigorously speaking, a catalytic action under the old definition, but the first has the characteristic earmark that the action proceeds proportionally to the concentration of a component (the positive ester ion) which is formed in minute amount (1/100,000 mols.) by a combination of the ester with the catalyzer, acted upon, formed again, and so forth, in infinite alternate reactions. As soon as we had completed this last experimental link, we started publishing our results.

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[1] Kastle, Euler, Acree, Lapworth.

[2] Bredig: *Loc. cit.*, **10**, 586; and Walton: Z. physik. Chem., **47**, p. 209–10, which is recommended to Mr. Acree's serious consideration. *Vide* also Abel: Z. Elek. Chem. **13**, 556.

[3] St. Louis address, *loc. cit.*, p. 278 · THIS JOURNAL, **39**, 30, 57, and 63.

Professor Bredig, one of the most brilliant investigators in the field of catalysis, suggested in 1903, I find, that the rigorous definitions were too narrow, and was disposed to consider as catalyzers all substances which increase the velocity of a reaction without there always being a "stoichiometrically equivalent" relation between the amount of the catalyzer transformed and the amount of the other reacting substance, the so-called "substratum" which is changed. Bodenstein, of the Leipzig school, stated that he expressed the same idea by saying that the catalyzer must not appear in the "gross equation" of the reaction, *e. g.*, in

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[1] Equations (6) and (32) THIS JOURNAL, 39, pp. 35 and 49.

[2] Z. Elek. Chem. 9, 996 (1901).

[3] *Vide* also Stieglitz: *Loc. cit.*, pp. 62-3.

$$2SO_2 + O_2 + H_2O \longrightarrow 2H_2SO_4.$$

Even such definitions, though much more in harmony with the real facts, appear too narrow, they would hardly include all the transformations of the imidoesters—and yet chemically, mathematically, and theoretically, the fundamental mechanism and mode of catalysis are the same in these cases as in the others. Bredig's own investigations have also been limited, it appears, to the perhaps more interesting and important old-style catalytic phenomena.

The proposed formulation will therefore be only an extension of the old definition, for homogeneous solutions, to make it include all these analogous actions. We will try to embody in it so much also of Euler's fundamental views as seems justified on the basis of experimental results, including our own. It may be that I have overlooked other efforts in this direction —in that case I shall be glad to be a cordial second or third. I have tried to find the same thing in Euler's writing, and perpaps, by implication, it may be found there; but the fact that be also limited his own work to truly catalytic actions (old style), *viz.*, esterification and saponification, in a most unfortunate and unsuccessful way, makes me think that experimental work of this nature, leading to the generalization described, may be of some little help and interest.

IV. A Question of Tautomerism.

"While there I[1] invited Mr. Stieglitz to collaborate with me (on tautomerism and *not* on catalysis) for our mutual benefit, as he had published a paper[1] on tautomeric compounds in which some wrong[2] ideas were advanced."[3] When I read, to my surprise, in Mr. Acree's article on tautomeric compounds in 1907 that I had expressed "wrong ideas" in an article on the theory of indicators I passed the assertion over in contemptuous silence, first and foremost because the allegation was not true, the wrong ideas being wholly the creation of Mr. Acree's imagination, and secondly it seemed foolish to protest against such a trivial matter. But since Mr. Acree has seen fit to refer to it as representing the subject of our conversation[4] in the summer of 1905, I will ask leave to present here the *printed evidence in the case*—nothing more. Briefly stated, the "wrong ideas" were that I had overlooked the ionization and salt formation of the phenol groups in the phenolphthalein reactions. Mr. Acree expressed that criticism in magnificent diagrams, covering more than two valuable pages of THIS JOURNAL. I shall ask permission to reproduce here a sufficient number of them in the more humble garb used in my original paper—they express the same ideas just as clearly.

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[1] Acree: THIS JOURNAL, **39**, 155 (1908).

Mr. Acree:[5] "Julius Stieglitz and others believe that in substances of the phenolphthalein type, the equilibrium may be expressed by the equations:

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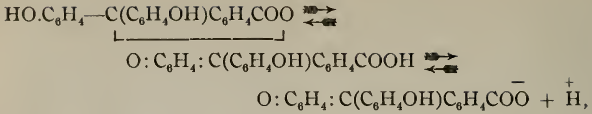
[1] J. Am. Chem. Soc., **25**, 1119.

[2] THIS JOURNAL, **37**, 72 (1907).

[3] Acree: *Ibid.*, **39**, 155 (1908).

[4] I suppose I was in error in assuming that Mr. Acree meant to imply that he "came" to Chicago "to get my methods;" but he certainly told me the day he came, that he *wanted to get my methods* (it pleased me at the time, that is why I have remembered it), and we spoke of my work with Upson, that had been published the year before, and of my work on the imidoesters. He was told that there was nothing particularly new in our experimental devices, the guiding underlying ideas forming the only important points. He has acknowledged that he used the privilege granted him and discussed our results with Dr. Schlesinger; no one can estimate the power of suggestion and encouragement lying perhaps unconsciously in the knowledge of such completed and successful work for a mind like Acree's to use the same principles and, perhaps unconsciously, do analogous work; and, as a matter of history, as was shown in the text, Mr. Acree's work after that, in many respects so strikingly like my own, bears no resemblance whatever in material, method, or principles to his earlier work on catalytic actions—a fact which his own unwise attempt to connect the two against the evidence of the printed records emphasizes more than any argument I could make. See above, page 406.

[5] *This Journal.*, **37**, 72 (1907).



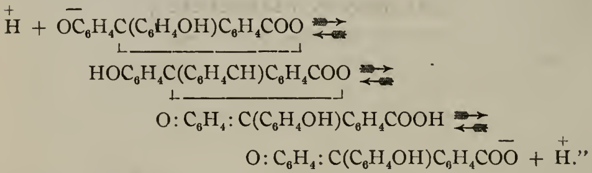
$$\mathrm{HO.C_6H_4{-}\underbracket{C(C_6H_4OH)C_6H_4COO}} \rightleftarrows \mathrm{O\!:\!C_6H_4\!:\!C(C_6H_4OH)C_6H_4COOH} \rightleftarrows \mathrm{O\!:\!C_6H_4\!:\!C(C_6H_4OH)C_6H_4CO\overset{-}{O}} + \overset{+}{\mathrm{H}},$$

and that the simple salts have the constitution

$$\mathrm{O\!:\!C_6H_4\!:\!C(C_6H_4OH)C_6H_4COOM.}$$

"They see in such an assumption the explanation of the color changes in indicators of this type.**[1]

"The writer[2] feels, however, that such an explanation is inadequate and that the following equations are more in harmony with the known facts:



$$\overset{+}{\mathrm{H}} + \mathrm{\overset{-}{O}C_6H_4\underbracket{C(C_6H_4OH)C_6H_4COO}} \rightleftarrows \mathrm{HOC_6H_4\underbracket{C(C_6H_4CH)C_6H_4COO}} \rightleftarrows \mathrm{O\!:\!C_6H_4\!:\!C(C_6H_4OH)C_6H_4COOH} \rightleftarrows \mathrm{O\!:\!C_6H_4\!:\!C(C_6H_4OH)C_6H_4CO\overset{-}{O}} + \overset{+}{\mathrm{H}}.\text{"}$$

There are more pictures to the same effect.

Mr. Stieglitz:[3] I explained the COLOR CHANGES correctly as expressed in equations and formulae down to the point marked with a double asterisk. *And in addition to that I wrote as follows* in discussing the conditions of equilibrium *quantitatively*:[4] "In this expression[5] for an aqueous solution of phenolphthalein, C_Q and C_H are not equal to each other, as hydrogen ions are formed not only by the carboxyl group of the quinoid acid *but also by its phenolhydroxyl group as well as by the two phenolhydroxyl groups of the lactoid acid.*[6] The effect of this increase of hydrogen ions is to make phenolphthalein, as indicator, react as a still weaker acid than it otherwise would, that is, it is less sensitive to alkalies, more sensitive to acids. Thus phenolphthalein is affected favorably in the very direction in which it is of particular value as an indicator. A most instructive quantitative study of similar relations has been carried out for carbonic acid by H. N. McCoy: Am. Chem J., 29, 437 (1903).”[1]

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[1] Asterisks mine, see below, my statement.

[2] Acree.

[3] The Theories of Indicators, *loc. cit.*

[4] *Loc. cit.*, foot-note, p. 1122. See also p. 1126.

[5] $C_{Q(uinoid)} \times C_H = k \times C_{L(actoid)}$.

[6] Italics new.

I believe I express in seven terse lines all and more than all that Mr. Acree tries to say in two pages of wonderful diagrams, which are intended to bring out as new the aged fact that phenols are weak acids and form salts. Further comment is superfluous, especially in regard to the credibility of a “mutual benefit” conversation about “tautomerism.”[2]

January, 1908.

see errata
p. 823

STUDIES IN BROMINATION.

By ~~T.~~ J. B. Cohen and W. E. Cross.

The communication by Messrs. Acree, Johnson, and Nirdlinger, which appeared in the December issue of This Journal, might be taken to imply that our investigation on the above subject had been anticipated by these gentlemen. If this is the implication we cannot for a moment admit it.

Messrs. Acree and Johnson have carried out an investigation which has led them to formulate views (not entirely original, as it now appears) on the subject of catalysis.

It happens that the addition compounds of the amides with bromine, which we have succeeded in isolating and of which we published an account in the Proceedings of the Chemical Society in May last, agree with the theories of Messrs. Acree and Johnson.

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[1] In this connection I must ask my friend, the author of the “Elements of Physical Chemistry” (1907), where Mr. Acree gives any new quantitative evidence of the correctness of this theory of indicators. I would earnestly suggest to him to read for himself his colleague's original article, and to compare it with pp. 1122–3 of mine, as well as with McCoy: This Journal, **31**, p. 518 (1904). The only occasion on which I have spoken with Mr. Acree of phenolphthalein was in September, 1907 (!) when I stated casually that I thought of investigating the possible rôle of intramolecular quinhydrone combinations as affecting the colors of phenolphthalein, rosanilines, and similar bodies. If I had thought at the time of his trivial criticism, I would have spoken of it and saved him from his *faux pas* in his last article.

[2] It has been my desire to be absolutely fair to Mr. Acree and in pursuance of that same purpose, since he has once committed himself in print, the manuscript of this article will be submitted to him before publication for the correction of any unconscious errors, if the facts warrant it. In future I cannot lose any more time in correcting him.

In accordance with the request of the writer of this article, the manuscript has been submitted to Professor Acree, and he will make a short reply in the April number of This Journal. Editor.

But Messrs. Acree and Johnson never attempted to obtain these compounds; they never even suggested that they might be prepared or that they intended to prepare them; they merely conjectured that such addition compounds were formed, "present in only a very small amount at any moment," in a reaction which is fundamentally different from the one we used.

The equation (1) which they bring forward in the December note and which they allege to have been taken from previous papers is not to be found in any of the references they give and is clearly an afterthought suggested by our experiments.

Even the second of their papers, which appeared several months after the publication of our notice, contains no reference to the formation of these compounds by our method. It is only quite recently that the authors seem to have become aware of our investigation and to have attempted to obtain addition compounds of basic substances with the halogens.

The pretext which they now advance for entering the field of investigation cannot be justified even by a stretch of etiquette which we do not feel disposed to entertain.

THE UNIVERSITY LEEDS.

REVIEWS.

DIE CHEMISCHE ANALYSE. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen, und physikalisch-chemischen Analyse. Herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der deutschen Technischen Hochschule Brünn. BAND I. DIE ANWENDUNG DER HYDRAZINE IN DER ANALYTISCHEN CHEMIE. Von PROF. DR. JULIUS SCHMIDT. pp. 92. Price, M. 3. BAND II. DIE UNTERSUCHUNGSMETHODEN DES ZINKS UNTER BESONDERER BERUECKSICHTIGUNG DER TECHNISCH WICHTIGEN ZINKERZE. Von DIPL. ING. H. NISSENSON, Direktor des Zentral-Laboratoriums der Akt.-Ges. für Bergbau, Blei- und Zinkfabrikation zu Stolberg und in Westfalen. pp. 140. Price, M. 4. Stuttgart: Ferdinand Enke. 1907.

These two monographs are the first of a series, to be published under the general title "Die chemische Analyse," which is to claim a position with respect to analytical chemistry which Beilstein's Handbuch occupies in organic, and Dammer's Handbuch in inorganic or technical chemistry, and to take the place of a large text-book on the subject, for which, in the opinion of the editor, the time is not ripe, owing to the present imperfections of our knowledge of some of the more recently developed phases of our science. The collection is to be comparable with the well-known "Sammlung chemisch und chemisch-technischer Vorträge." The monographs will cover special topics and important procedures in chemical analysis, and each is intended to be complete in its field. The material is to be critically reviewed by the author, and only such articles as contain valuable procedures are to be mentioned in detail; others, when referred to at all, will be briefly dealt with and the reasons, as far as known, why the methods have not been found useful will be stated. The subject matter will also be arranged and presented with reference to the value of the monographs to advanced students, as well as to practicing chemists and investigators. The titles of more than forty proposed monographs are given, and these, with the names of their authors, give promise of much varied, interesting, and valuable material, including especially the applications of the results of researches in physical chemistry to analytical chemistry, which are of primary importance in the progress of this branch of chemical science.

In the first volume of the series Dr. Schmidt, after some introductory matter, deals first with the use of hydrazine and its salts in quantitative analysis (Chapter I.), and then in qualitative analysis (Chap. II.); this is followed by the uses of phenylhydrazine for analytical purposes (Chap. III.), the uses of the substitution products of phenylhydrazine as reagents (Chap. IV.), and (Chap. V.) the uses of other derivatives of the hydrazines, especially the acid hydrazines. At the close of the monograph an apparently exhaustive bibliography of the literature of the subject is given.

The author of the second volume was charged by the International Committee on Analysis of the Fifth International Congress of Applied Chemistry with the study of the technical methods for the determination of zinc and made a report to the sixth Congress at Rome. He now brings together in this monograph a compilation and review of all the published procedures which appear to have any value. After some introductory statements, he considers the qualitative tests for zinc, and then divides his discussion of quantitative methods into (I.) volumetric methods, (II.) electrolytic methods, (III.) gravimetric methods, (IV.) special methods of separation, and (V.) methods applicable to particular cases, such as the analysis of metallic zinc, zinc dust, flue dust, cinders, alloys, ores, organic zinc compounds, the determinaion of zinc in food-stuffs. While no bibliography is appended, there are abundant references to original papers and these indicate that the author has examined a wide range of journal literature.

Analysts have for some time desired some new, comprehensive, and authoritative work for their guidance. This desire has been in part met by some of the more recent works, but not to complete satisfaction. This projected plan of issuing these monographs, each presumably prepared by some one selected because of his familiarity with the field which he is asked to cover, seems, of itself, to afford excellent promise of valuable assistance, and this is, in general, borne out by the two volumes under review. It is obvious that, with so much material to review critically and to condense into a comparatively small space, there must be excellent judgment displayed if the result is not to be a mere cataloguing of processes on the one hand, or an uneven treatment of the various procedures on the other. On the whole, the work of these two monographs appears to have been well done. The reader must expect to find them chiefly useful as affording an excellent general review of the present status of our knowledge regarding particular procedures or topics, and must expect to be often disappointed if he searches for the more minute detail of procedures and experiments in these pages. Indeed, the reader will doubtless often wish that a little more had been given in particular cases, but the many references to original papers make a further search for detailed directions comparatively easy.

This publication appears to the reviewer to be an important addition to chemical literature and one which, if it justifies its present promise, deserves the interest and support of all analysts who desire to be in touch with the recent advances in that branch of chemistry. H. P. TALBOT.

CLEAN WATER AND HOW TO GET IT. By ALLEN HAZEN, Member of the American Society of Civil Engineers, Etc., Etc. First edition, first thousand. New York : John Wiley & Sons. pp. 178. Price, cloth, $1.50.

Mr. Hazen's book is interesting and valuable to every citizen, and especially valuable to those who have a voice in the construction and maintenance of water supply, but are neither chemists nor engineers; to mayors and members of city governments.

The subjects discussed are: Water supply from lakes, from rivers, from ground water; action of water on iron pipes;

methods of purifying water; storage of filtered water; construction of water works; and financial management. E. R.

PRACTICAL CHEMISTRY FOR ARMY AND MATRICULATION CANDIDATES AND FOR USE IN SCHOOLS. By GEOFFREY MARTIN, B.SC., PH.D., Lecturer and Demonstrator in Chemistry at University College, Nottingham; author of "Researches on the Affinities of Elements," "Ueber das Affinitätsgesetz in dem periodischen System," Etc. London: Crosby Lockwood & Son. 1907. pp. 144. Price, 2 shil.

This book is evidently intended to be used as a laboratory guide in connection with a lecture course or as a guide by those who are familiar with the theory, but have had no practical laboratory work. The first 37 pages are devoted to the preparation and properties of the common gases, while the balance of the book deals largely with quantitative chemistry and analytical operations. In this part of the book the reactions are not those which would lead to any systematic knowledge of the subject, but are selected to bring out some special method or principle of analytical chemistry.

This book could not be used to advantage in any schools in this country and has probably been prepared to supply a need in the case of men who are required to pass examinations for special positions. It could be used neither for beginners, for those who wish a thorough knowledge of the subject, nor for those who desire to learn enough analytical chemistry to fill positions as analysts. J. E. G.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. Third edition, revised and enlarged. New York: The Macmillan Co. 1907. pp. xi + 650. Price, $4.00 net.

This new and enlarged edition of Professor Jones's well-known text-book will be welcomed by teachers and students of physical chemistry. Unlike the second edition, which was a reprint of the first, the present (third) edition has been extensively revised, contains a large amount of new matter, and is a satisfactory realization of the author's aim, as stated in the preface, to bring the book up to date.

The volume has been increased in size by 85 pages, but the space devoted to new material is somewhat greater than this, a result made possible by judicious omissions. Subjects newly or more fully treated include J. J. Thomson's electron theory; radioactivity; the work of Morse, and of Lord Berkeley and E. G. J. Hartley, on the direct measurement of osmotic pressure; colloidal suspensions; hydrolytic dissociation; conductivity of fused salts; dissociation in nonaqueous solvents; catalysis; the author's hydrate theory; researches of the author and coworkers on conductivity and viscosity in mixed solvents.

The work of revision and of incorporating the new material with the old has been in the main conscientiously done, but a few inaccuracies have been overlooked. It is no longer correct, since the work of Nernst with the iridium Victor Meyer apparatus, to say, as on page 61, that no material for the inner tube is known which can be used at temperatures above 1800°. Nernst in 1903 measured vapor densities up to 2000°. The statement on page 90 that all known gases have been liquefied should be qualified by excepting helium. It would have been better, on page 202, to modify the statement that direct measurements of osmotic pressure have been made only with dilute solutions (less than one-fifth normal), since it is contradicted a few pages beyond by the description of the work of Morse and of Lord Berkeley.

Much more serious is the error on page 358, repeated in slightly different words on page 530, where the reader is told that heat energy is the product of temperature and quantity of heat. This is in no sense correct. A given change in heat energy may appear either as the product of temperature and change in entropy, or as the product of change in temperature and heat capacity, according as it is the "capacity factor" or the "intensity factor" which varies during the change. In neither case is the rôle of capacity factor played by a quantity of heat.

These slight defects, however, are far outweighed by the general merit of the book. The copious references to the literature, which have been greatly increased in number in the present edition, are an excellent feature, and will materially add to its value as a book of reference. For use as a text-book it is especially adapted to the needs of beginners, and presents decided advantages over most others of its class, owing to the fact that the author has aimed at clearness rather than extreme conciseness of statement. Though the field covered is quite broad, the treatment is elementary and readily intelligible throughout.

As a distinctly improved edition of an already widely used text-book, the work seems assured of a large measure of success.

R. G. VAN NAME.

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STUDIES IN CATALYSIS.

IV. THE CATALYSIS OF IMIDOESTERS.

BY IRA H. DERBY.

When an imidoester decomposes in an aqueous solution, at least[1] two reactions take place; in one the ester breaks down into a nitrile and an alcohol according to

$$RC(:NH)OR \rightarrow RCN + HOR \qquad (1),$$

and in the second one, minimal decomposition is affected through the agency of water, ammonia and an acid ester resulting according to

$$RC(:NH)OR + HOH \rightarrow RCOOR + NH_3 \qquad (2).$$

The velocity of the second reaction is enormously accelerated by the addition of an acid, much in the same way that the hydrolytic decomposition of an acid ester or cane sugar is accelerated in proportion to the concentration of the hydrogen ions of the acid added. According to Prof. Stieglitz[2] the latter, so-called catalytic, actions find their explanation simply in the formation of ionized salts of cane sugar and the esters with the added acid, in which the positive (oxonuim) ions of the organic compounds form the "active masses" which react with water; hence the action must obviously be accelerated in proportion to the increased concentration of these positive ions. These oxonium bases being so weak that exact measurements of the actual concentrations of their positive ions, under different conditions, by means of their affinity constants seemed for the time impracticable, the study of the parallel behavior of the closely related imidoesters was taken up, because all the necessary experimental data would be obtainable in this group.

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[1] An acid amide is very likely another by-product. The chief product is a nitrile. *Vide* Schlesinger's later paper.

[2] Report of the Congress of Arts and Science, St. Louis, Vol. IV., p. 276 (1904); THIS JOURNAL, **39**, 29 and 402 (1908). *Vide* also Bredig: Z. Elek. Chem., **9**, 118 (1903).

At the suggestion and under the direction of Prof. Stieglitz I took up the problems of ascertaining experimentally what component in the solution of an imidoester gives rise to the decomposition expressed in (1), and especially of determining the active component in the more important reaction expressed in (2), on which the presence of an acid has a markedly accelerating effect. The second, more important reaction will be considered first.

THE ACTION OF ACIDS ON IMIDOESTERS.[1]

When an acid is added to an imidoester a condition of equilibrium is established between the weak base and its salt according to

$$RC(:NH_2Cl)OR' + H_2O \rightleftarrows RC(:NH_2OH)OR' + HCl \quad (3).$$

The reacting constituent in the decomposition accelerated by the addition of an acid can very readily be ascertained, then, by the determination, first, of the velocity of the decomposition, and, secondly, of the concentration of each component of the system at any moment *t*, and by the application of the laws of chemical equilibrium and dynamics to the data obtained. The work resolved itself, then, (1) into the development of simple, rapid methods of analysis for following the velocity of the deomposition of the imidoesters by water, (2) into the determination of the hydrolysis constants in the equilibrium equation of the hydrolyzed salt (equation 3), that is, of the affinity constants of the imidoesters, from which the concentrations of the components of the system could be calculated, and (3) into the measurement of the velocities of decomposition of a number of imidoesters under various conditions.

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[1] For the theoretical and mathematical treatment of the problems reference is made to papers of Dr. Stieglitz, published in THIS JOURNAL. This paper is to deal only with the experimental work.

The Methods of Analysis.

The simplest method of following the decomposition of a salt into ammonium chloride and an acid ester, according to

$$RC(:NH_2Cl)OR + HOH \rightarrow RCOOR + NH_4Cl \qquad (2'),$$

was suggested by the fact that the free imidoesters of the aromatic acids are oils or solids which are usually rather difficultly soluble in water but easily soluble in organic solvents like chloroform or carbon tetrachloride. The second basic ingredient in the mixture, ammonia, is, on the other hand, exceedingly soluble in water and extremely little soluble in the organic solvents. It was found, in fact, that after the addition of an alkali like sodium hydroxide the two bases could be separated quantitatively from dilute solutions by means of carbon tetrachloride, which was given the preference because of its greater density and cheapness as compared with chloroform.

Two simple methods of analysis were based on this separation. The shorter one, which was most frequently used, is as follows: If the bases are liberated from these salts in a measured portion of the mixture represented by the expression (2′), by the addition of a measured amount (v_1 cc.) of tenth-normal alkali, and the free imidoester is removed by carbon tetrachloride, the alkali is neutralized by the acid of the imidoester salt, exactly as if it were free hydrochloric acid; but with the ammonium chloride the alkali simply sets free the equivalent amount of ammonia which remains quantitatively in the aqueous solution. If, after the removal of the free ester by extraction with carbon tetrachloride, the aqueous liquid is titrated to neutrality by use of tenth-normal acid (v_2 cc.), in the presence of an indicator (methyl orange) sensitive to ammonia, the difference between the volume of the standard alkali and acid used ($v_1—v_2$) represents the alkali neutralized by the acid of the ester salt. This quantity diminishes as the decomposition proceeds, ammonium chloride replacing the imido salt. In the actual work an aliquot portion (usually 25 cc.) of the solution under investigation was run into a measured excess (one and a half times the calculated amount) of tenth-normal alkali contained in a Squibb separatory funnel, the imidoester removed by three extractions with 20, 15, and 10, or 15, 10, and 5 cc. of carbon tetrachloride and the aqueous residue washed into an Erlenmeyer flask and neutralized in the presence of methyl orange. The accuracy of the method is shown by the results given in Table I., in which the weight of imidoester salt used for analysis is given in the first column, the weight of ammonium chloride mixed with the imidoester salt taken is given in the second column, and the actual volume of tenth-normal alkali used to neutralize the acid from the imidoester salt and the calculated amount required for the neutralization are listed in columns three and four, respectively. Ammonium chloride was added in the amount in which it was likely to be present in actual work in order to prove that within the limits of accuracy desired no ammonia is lost by the carbon tetrachloride extraction.

Table I.— Hydrochloride of Ethyl Imidobenzoate.[1]

Ester salt.	Ammonium chloride.	$v_1 — v_2$ used.	$v_1 — v_2$ calculated.
....	0.096	0.02	0.00
....	....	0.03	0.00
0.2313	....	12.28	12.45
....	0.070	0.22	0.00
....	0.070	0.14	0.00
0.1940	....	10.40	10.45
0.2046	....	11.05	11.07
0.2058	0.098	11.00	11.14
0.1252	0.039	6.74	6.74
0.0573	0.061	3.15	3.08
0.0409	....	2.16	2.20

The other and longer method of analysis is based on the same general principle as the one just given, but differs from it in that the imidoester base is determined directly. The imidoester was taken up from the combined carbon tetrachloride extract by shaking this with a measured excess (two or three times the calculated amount, in two successive portions) of tenth-normal sulphuric acid, and then the excess of acid neutralized by standard alkali in presence of an indicator (methyl orange or alizarinsulphonate) sensitive to the imidoester base. The carbon tetrachloride was washed with water after two extractions with the standard acid and the aqueous and acid extracts were mixed and titrated. As the imidoesters are much weaker bases than ammonia, methyl orange is not as sensitive to them as to ammonia, and the hydrochlorides of the esters react very slightly acid to methyl orange; so slightly that they produce in moderate dilutions, not strong acid tints (pink or red), but a brownish-pink color. A standard color of this tint was made for comparison and used for the end point in the titrations. For very accurate work standard tints were made for the various concentrations of salt used, since the degree of hydrolysis (equation 3) depends, of course, on the dilution. This last precaution was rarely necessary. While the method is longer and less convenient than the first one described, it was useful especially in determining the velocities of decomposition of the imidoester salts in the presence of added excess of the imidoester base. The degree of accuracy of the method is shown by the results given in Table II. The data in the various columns have the same significance as in Table I., except that in columns three and four the volumes are of tenth-normal acid instead of alkali.

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[1] Check analyses were made with all the imidoesters used but will not be reported. The method was always reliable for the aromatic esters.

Table II.—Hydrochloride of Ethyl Imidobenzoate.

Ester salt.	Ammonium chloride.	$v_1 - v_2$ used.	$v_1 - v_2$ calculated.
0.2313	....	12.27	12.45
....	0.070	0.10	0.00
....	0.070	0.12	0.00
0.1940	....	10.42	10.45
0.2046	....	11.02	11.07
0.2058	0.099	111.10	11.14
0.1252	0.039	6.78	6.74
0.0573	0.061	3.30	3.08
0.0409	....	2.30	2.20

PREPARATION OF THE IMIDOBENZOIC ESTER HYDROCHLORIDES AND IMIDOBENZOIC ESTERS.

The Imidoester Hydrochlorides.

Particularly pure imidoester salts being desired for these determinations, their preparation by Pinner's general method, with certain modifications, will be briefly described.

According to the method of Pinner[1] they were prepared by mixing equimolecular amounts of the carefully purified and dehydrated nitrile and alcohol and saturating the mixture, at 0°, with dry hydrogen chloride. The reaction

$$RCN + ROH + HCl = RC(NH_2Cl)OR \qquad (4)$$

results after a few hours' standing. By this process a very hard, crystalline mass is obtained which it is difficult to break up and still harder to free from the excess of hydrochloric acid. If, however, three or four times their volume of dry ether is added to the mixed nitrile and alcohol and the whole is then saturated with hydrogen chloride, the resulting salt is loosely, finely crystalline, easily handled and purified. The yield is not diminished, for most of the imidoester salts are quite insoluble in ether. The product was purified by filtering off the crystals and washing them with dry ether, after which the salt was kept for some time under reduced pressure in a vacuum desiccator so that all ether and free hydrochloric acid might be removed. To obtain a perfectly pure product, further processes were resorted to in special cases and will be described in those connections. These salts are thus easily prepared in quantity but are difficult to keep, since traces of moisture produce decomposition, and by long standing even the dry salt very slowly undergoes spontaneous decomposition. Two of the products of decomposition were easily shown to be ammonium chloride and benzamide by the following methods: Ammonium chloride is nearly insoluble in absolute alcohol while the imidoester hydrochlorides are freely soluble. A sample of the imidoester salt, which had stood for some time, left a considerable amount of a white, crystalline residue after the imidoester had been dissolved out by absolute alcohol. A portion of this white residue, after drying, gave, on analysis, 66.06 per cent chlorine instead of 66.22 per cent, the theoretical amount for ammonium chloride. The alcoholic solution was evaporated *in vacuo*. An ether extract of the crystalline residue gave a substance which melted at 125°, while benzamide melts at 128°.

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[1] Pinner: The Imidoesters.

The Imidobenzoic Esters.

Imidobenzoic ester hydrochlorides, when treated with alkali hydroxide in cold solutions, yield immediately the imidobenzoic ester and an alkali chloride according to this general reaction:

$$RC(NH_2Cl)OR + MOH \longrightarrow RC(NH)OR + MCl + H_2O.$$

These imidoesters are colorless, highly refracting oils, or white to pale yellow solids heavier than water and little soluble in that medium, but readily soluble in alcohol and ether. The general method of preparation finally adopted was as follows, preliminary experiments having shown that the preparation of pure esters is accompanied by many difficulties. Into a separatory funnel was placed sufficient of a 5–10 per cent sodium hydroxide solution for the complete decomposition of the imidoester salt, ether was added, and the whole cooled in ice water. The cooling minimizes the decomposition of the salts. To this cold solution the solid imidoester hydrochloride was added in successive small portions while the mixture was constantly agitated to facilitate the extraction of the liberated imidoester by the ether layer. The extract was then treated with fused calcium chloride in sticks and allowed to stand for an hour or more, usually in ice water. The mixture was shaken frequently to insure drying of all parts of the ether solution. Finally the ethereal solution was siphoned from the drying agent through a dry filter into a dry flask, when the drying process was again repeated and followed by one or two more repetitions. The success of the preparation and the purity of the final product depends very much on the thorough removal of the water from the ether solution. The ether was then driven off by distillation over a water bath and the residue, if an oil, was fractionally distilled *in vacuo*;

if a solid, it was purified by recrystallization. All the esters, on standing, even in sealed tubes, decompose to a greater or less extent, and long, colorless, highly refracting, prismatic crystals separate from the liquids. In all the work where pure substances were necessary, freshly prepared esters or recently distilled portions were always used. The imido-esters were always analyzed by titrating a weighed amount, mixed with 25–30 cc. water, directly with tenth-normal acid (usually sulphuric acid) in the presence of methyl orange, that tint of red being used as the end point which was most nearly like the tint produced by a corresponding weight of the pure imido hydrochloride when dissolved in the same volume of water with the addition of an equal amount of methyl orange.

Ethyl Imidobenzoate.

Ethyl imidobenzoate was made and analyzed as described above. The following table shows the boiling points of several preparations, with the accompanying analyses. Column one shows the boiling point; two, the corresponding pressure; three, the weight of the ester taken for analysis; four, the amount of tenth-normal acid used; and column five, the calculated volume of tenth-normal acid required for the same weight of pure substance.

Boiling point.	Pressure in millimeters.	Weight of esters.	Acid used.	Acid calculated.
115°.5	....	0.2902	19.42	19.46
115°	21.5	0.4319	28.92	28.96
115°	21.5	0.4048	27.14	27.14
101°–102°	11.0	0.2402	16.13	16.10

The boiling point at 744.7 mm. pressure was 219°. The boiling in this case was accompanied by slow decomposition, as was shown by analysis of the sample.

The pure product was a colorless, somewhat viscous liquid more dense than water and having an index of refraction of 1.5278 at 20°; it is miscible in all proportions with alcohol and ether, but only very slightly soluble in water. At 25° 100 cc. of aqueous solution was found to contain 0.396 gram of ethyl imidobenzoate, or a liter will dissolve 0.026 molecule.

The ester is soluble in carbon tetrachloride and three determinations were made to find out its partition coefficient between water and carbon tetrachloride, with the following results: C_1 and C_2 indicate the amounts of imidoester dissolved in 100 cc. of each solvent, respectively, while $K = C_2/C_1$ shows the partition coefficient. The temperature was 23° (±1°).

C_1.	C_2.	C_2/C_1.
0.0194	2.450	126
0.0114	1.464	128
0.0073	0.901	123

Methyl Imidobenzoate.

This substance, prepared by the method described, was obtained pure with much greater difficulty than was experienced with any of the other esters studied, and when it was obtained pure it soon changed, so that frequent fractional distillations were necessary to prepare and keep sufficiently pure material for the work.

The following table is in every respect similar to the one given in connection with the ethyl ester. It shows the results obtained with the methyl ester.

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
104°	20.5	0.4000	29.46	29.60
83°	5.8	0.3554	15.67	15.64
106°	22.0	0.2724	20.05	20.15
107°	22.5	0.2680	19.80	19.83
91°.8	11.0	0.2528	18.72	18.69
....	....	0.2097	15.43	15.40
101°	18.0	0.4862	35.81	35.98
98°	14.5	0.4227	31.27	31.28
99°.7	16.5	0.4202	31.07	31.09
75°.5	3.8	0.3171	23.51	23.47

The properties of the methyl ester differ from those of the ethyl ester only in degree. It is slightly more soluble in water. The index of refraction at 20° is 1.5430. At 10.5 mm. pressure the boiling point is 10° lower than that of the ethyl ester at the same pressure.

Normalpropyl Imidobenzoate.

This ester was prepared by the general method and analyzed in the usual way. It was obtained pure more readily than any of the other esters studied. The tendency to form benzamide was much less pronounced, as indicated by the very slight amount of solid residue remaining in the flask after the distillation *in vacuo*.

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
121°	16	0.1836	11.25	11.25
121°.1	16	0.2757	16.97	16.90
121°	16	0.2718	16.74	16.66

The normalpropyl ester appeared to be less soluble in water than its two homologues just described, but resembled them closely in properties. The index of refraction, as determined at 20°, was 1.5173.

Isopropyl Imidobenzoate.

The isopropyl ester was prepared like the other esters. It was obtained pure with much more difficulty than its isomer and, like the methyl ester, seemed to decompose somewhat into benzamide, a residue of which was usually obtained after the fractional distillation of the ester *in vacuo*. The boiling points under the reduced pressures, together with the analytical results, are given in the table:

Boiling point.	Pressure in millimeters.	Weight of ester.	Acid used.	Acid calculated.
102°	10	0.2106	12.80	12.90
106°	13	0.2239	13.66	13.72
....	..	0.2110	12.93	12.95
114°	20	0.2127	13.05	13.04
114°	19	0.2139	13.13	13.11

The properties were the same as for the isomeric normalpropyl ester. A rough determination of solubility at room temperature (about 21°) showed that 100 cc. of solution contained 0.161 gram of the ester. The index of refraction, at 20°, was 1.5144.

Methyl Metanitroimidobenzoate.

The free ester was prepared from the hydrochloride salt by the general method. It forms a solid.

This solid was pale yellow in color and very slightly soluble in water. It melted sharply at 50°.6 and was used for the experimental work to be described later. As is shown by its conductivity in aqueous solution at 25°, it contained nothing of such a nature as would vitiate the results. This conductivity was 4×10^{-6}.

THE AFFINITY CONSTANTS OF IMIDOESTERS BY THE CONDUCTIVITY METHOD.

The apparatus used for the work was of the kind ordinarily used in conductivity measurements; namely, a meter-wire bridge and resistance box, both of which were carefully calibrated, a specially wound induction coil, and a sensitive telephone. In some of the later work a short bridge was used. The scale on this was laid out in proportional parts. This was found sufficiently accurate for the work and much more convenient than the meter bridge. For maintaining a condition of constant temperature a large, rectangular, galvanized water bath, of about one cubic meter capacity and jacketed with asbestos, was fitted with a very large (about one liter) gas thermoregulator of the Ostwald type, filled with toluene. The water was kept thoroughly stirred by means of a four-armed, windmill-shaped stirrer run by an electric motor. After once being adjusted to 25°, this bath remained at a uniform temperature day and night for weeks, varying much less than 0°.01, as was shown by a series of observations made with a Beckmann thermometer. The level of the water in the bath was maintained constant by occasional additions so that the hydrostatic pressure exerted upon the regulator might be uniform. For the conductivity work at 18° a bath fitted up similarly to the one just described was used, except that in this case a cold water coil was essential to keep the water sufficiently cooled to enable the regulator to work.

Since the imidoester salts, when brought into water solution, instantly begin to decompose, the ordinary method for obtaining the various concentrations, by means of successive dilutions of a concentrated solution of the substance, could not be used. Each solution investigated was made up separately by weighing the amount of salt required for 50–100 cc. of solution. This weighed amount of substance was then transferred to the dry Arrhenius cell, which had already been in the bath long enough to acquire the proper temperature, and the water for the solution, which was also at the bath temperature, was poured in. The salts are rapidly soluble, and when the electrodes were put in after the addition of the water and raised and lowered five or six times a homogeneous solution was obtained. During the time (never less than two minutes) required for the preparation of the solution, some change inevitably takes place and the first bridge reading corresponds, then, to the mixed solution of imidoester and ammonium chloride formed by the decomposition and not to the pure solution of imidoester hydrochloride, which could only be observed at zero time, a practical impossibility in this case. For getting this reading corresponding to zero time, a process of extrapolation was used. An inspection of a large number of series of measurements showed that during the first twenty or twenty-five minutes the changes in conductivity, consequently the change in bridge reading, was proportional, within the limits of experimental errors, to the time. For any given experiment, then, the exact time at which the water was poured in was noted, at the end of five minutes the first bridge reading was taken, followed by three or four more readings also at five minute intervals. From these bridge readings a simple numerical extrapolation gave the desired reading at zero time. An actual series of observations are here given to clearly illustrate this very important detail of the method. The columns in the following table have this significance: One shows the time in minutes; two, the bridge readings taken at the times given; three, the changes in bridge readings for each interval of five minutes and also the average; four, the total changes in bridge reading corresponding to each total time as calculated by means of the average difference found from column three; and column five gives the zero-time readings of the bridge as calculated from each observed reading by adding the calculated corresponding total variations given in column four.

Time.	Bridge. Required.	Bridge difference.	Calculated total variations.	Bridge reading at zero time.
0	......	..	..	......
5	0.449	..	4	0.453
10	0.445	4	8	0.453
15	0.440	5	12	0.452
20	0.437	3	16	0.453
25	0.434	3	20	0.454
	Average,	4	Aver. for zero time,	0.453

The bridge reading corresponding to zero time, was, then, 0.453, and was used, together with the resistance and constant of the cell, to derive the specific conductivity of the solution at the instant of preparation. Another method by which the conductivity at zero time was obtained consisted in calculating each specific conductivity corresponding to each bridge reading and using these values in place of the bridge readings for the extrapolation calculation. This involves more calculations than the first method and, since the resulting values are nearly the same, the former method was most used.

THE HYDROLYSIS CONSTANTS FOR THE IMIDOESTER HYDROCHLORIDES.

Ethyl Imidobenzoate.

The data for the hydrolysis constant for the hydrochloride of ethyl imidobenzoate (equation 3) were determined, as described above, by Bredig's method.[1] The molecular conductivities, μ_v, for the nonhydrolyzed salt were first determined, the hydrolysis being suppressed by the addition of an excess of 0.025 and 0.0125 mole of free base. Two series of determinations were made and the results of these are summarized in Table III. Column one gives the volume in liters containing a gram molecular weight of the salt; columns two and three, the molecular conductivities, μ_v, in reciprocal mercury units, in the presence of 0.025 and 0.0125 mole, respectively, of free base; and columns four and five, the conductivity, μ_∞, of the nonhydrolyzed salt for infinite dilution, as calculated from the previous columns by the addition of the characteristic constants, Δ_v, of Ostwald and Bredig.[1]

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[1] Z. physik. Chem., **13**, 288 (1894).

Table III.

V.	0.25 base. μ_v.	0.0125 base. μ_v.	0.025 base. μ_∞.	0.0125 base. μ_∞.
32	83.4	83.2	97.4	97.2
64	86.5	87.5	97.5	98.5
128	90.3	89.5	98.3	97.5
256	92.7	92.4	98.7	98.4
		Mean,	97.97	97.90
32	83.5	83.4	97.5	97.4
64	86.1	86.9	97.1	97.9
128	89.2	89.7	97.2	97.7
256	91.7	92.7	97.7	98.7
		Mean,	97.37	97.9

The agreement in the values for μ_∞ being satisfactory, both as regards the values obtained in the presence of varying amounts of free base and as regards the duplicate series, the following mean values were considered to represent the true molecular conductivities of the nonhydrolyzed salt at 25° (±0°.01):

V	32	64	128	256
μ_v	83.4	86.7	89.6	92.4

The conductivity of the hydrochloride was next determined in the hydrolyzed solution, without the addition of any free base, and the degree of hydrolysis calculated according to

$$x = \frac{M_{obs} - \mu_v}{\mu_{HCl(v)} - \mu_v},$$

in which M_{obs}, μ_v and $\mu_{HCl(v)}$ represent the molecular conductivities of the hydrolyzed salt, the salt, and hydrochloric acid, respectively, all referred to the same volume, the volume containing a molecular equivalent of total electrolyte.[1] The values which were used for the molecular conductivity of hydrochloric acid at 25° were those determined by Ostwald:

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[1] *Loc. cit.* In later determinations (*vide* a later paper by E. E. Barnard) a more exact graphic method was used to obtain μ_∞.

V	32	64	128	256	512
μ_{HCl}	369	374	376	378	379

Table IV. summarizes the results. Column one gives the volume, in liters, containing a gram molecule of the salt; two shows the observed molecular conductivity for the hydrolyzed salt; three, the degree of hydrolysis; and column four, the hydrolysis constant calculated from

$$\frac{(1-x)V}{x^2} = \frac{k_{base}}{k_{H_2O}} = K_{hydrolysis}.$$

Table IV.

V.	$M_{obs.}$	$100x$.	$10^{-5} \times K_{hydrolysis}$.
32	85.1	0.59	9.1
32	85.1	0.58	9.5
64	89.7	1.04	5.8
64	89.4	0.94	7.2
128	93.1	1.20	8.8
256	96.3	1.36	13.0
			Mean, 8.9×10^5

The affinity constant for ethyl imidobenzoate is then:

$$K_{aff.} = K_{hydrolysis} \times K_{H_2O} = 8.9 \times 10^5 \times 1.2 \times 10^{-14} = 1.1 \times 10^{-8}.$$

Methyl Imidobenzoate.

The experimental results for the determination of the constant for the hydrochloride of methyl imidobenzoate are given in Tables V. and VI. Table V. gives the data for the determination of the molecular conductivity of the nonhydrolyzed salt at various dilutions and the columns have the same significance as in Table III.

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[1] Stieglitz and Derby: This Journal, 31, 449 (1904).

Table V.

V.	0.25 base. μ_v.	0.0125 base. μ_v.	0.025 base. μ_∞	0.0125 base. μ_∞
32	....	85.3	....	99.3
64	89.3	89.9	100.3	100.9
128	91.5	92.1	99.5	100.1
256	....	95.0	....	101.0
		Mean,	99.9	100.7
32	....	86.7	....	100.7
64	89.9	90.7	100.9	101.7
128	92.7	92.9	100.7	100.9
256	....	94.3	....	100.3
		Mean,	100.8	100.8

The mean of all of the values for the conductivity at infinite dilution was 100.5. The following values were taken as representing the molecular conductivities of the nonhydrolyzed salt:

V	32	64	128	256	512
μ_v	86.5	89.5	92.5	94.5	96.5

Following are the graphically interpolated values for intermediate dilutions corresponding to the four odd dilutions listed in Table VI.:

V	29.4	58.8	117.6	235.2
μ_v	86.1	89.0	91.8	94.2

Table VI. gives the observed conductivities of the hydrolyzed salt. The columns have the same significance as in Table IV.

Table VI.

V.	$M_{obs.}$	100 x.	$10^{-5} \times K_{hydrolysis}$.
32.0	89.7	1.13	2.47
32.0	89.7	1.13	2.47
32.0	89.5	1.05	2.87
64.0	93.6	1.44	3.04
64.0	93.8	1.47	2.91
64.0	93.6	1.44	3.04
58.8	92.3	1.16	4.32
128.0	97.8	1.87	3.59
128.0	96.6	1.80	3.88
128.0	97.8	1.87	3.59
128.0	97.5	1.76	4.06

Table VI—(Continued).

V.	M_{obs}.	$100x$.	$10^{-5} \times K_{hydrolysis}$.
117.6	97.4	1.97	2.97
256.0	101.0	2.29	4.77
256.0	99.9	1.90	6.94
256.0	100.9	2.25	4.94
235.2	100.8	2.33	4.23
512.0	104.2	2.70	6.83
			Mean, 3.93×10^5

The affinity constant for methyl imidobenzoate, as calculated from the hydrolysis constant, is 4.7×10^{-9}.

n-Propyl Imidobenzoate.

The following tables give the data for determining the hydrolysis constant of the *n*-propyl imidobenzoate. The significance of the columns is the same as in Tables III. and V. The amount of free base present was sufficient to suppress the hydrolysis but was not accurately weighed out in each case, as was done in the determinations on the ethyl and methyl esters. The values for μ_∞ were obtained by graphic interpolation.

Table VII.

V.	μ_v.	μ_∞.	v.	μ_v.	μ_∞.
32	82.4	96.4	128	88.1	96.1
48	84.0	96.2	192	89.1	95.9
64	85.4	96.4	256	91.1	97.1
96	87.3	96.5	384	91.6	96.0
					Mean, 96.3

Table VIII. gives the degree of hydrolysis and the value of the constant. The columns have the same significance as in Tables IV. and VI.

Table VIII.

V.	M_{obs}.	$100x$.	$10^{-5} \times K_{hydrolysis}$.
32	83.6	0.42	18.1
48	86.0	0.69	10.0
64	88.0	0.90	7.8
96	89.6	0.80	14.9
128	91.5	1.18	9.1
192	92.3	1.11	7.4
256	94.9	1.32	14.5
			Mean, 12.8×10^5

The affinity constant, as calculated from the hydrolysis constant, is 15.4×10^{-9}.

Isopropyl Imidobenzoate.

Tables IX. and X. give the results of the conductivity measurements for isopropyl imidobenzoate, the degree of hydrolysis, and the value of the hydrolysis constant:

Table IX.

V.	μ_v.	μ_∞.	V.	μ_v.	μ_∞.
32	82.0	96.0	256	90.1	96.1
64	85.4	96.4	512	91.7	95.7
128	88.1	96.1	407.3	91.5	96.2
				Mean,	96.08

Table X.

V.	M_{obs}.	$100\,x$.	$10^{-5} \times K_{hydrolysis}$.
32	83.6	0.56	10
32	84.2	0.76	6
64	87.3	0.65	16
128	90.6	0.86	17
256	93.0	1.00	25
256	93.8	1.28	15
512	96.5	1.66	18
407.3	96.2	1.63	15
		Mean,	15×10^{5}

The value of the affinity constant, as calculated from the hydrolysis constant, is 1.8×10^{-8}.

Methyl Metanitroimidobenzoate.

Because of the great rapidity of decomposition of this body, the conductivity determinations were carried out at a temperature of 18°. The free methyl metanitroimidobenzoate base was found to be much less soluble than any of those previously studied and, for the determination of the conductivities of the nonhydrolyzed salt, a sufficient quantity of base was added to each solution so that a little remained undissolved after the thorough mixing preceding the measurements. To be absolutely sure that all hydrolysis was suppressed, each solution was tested with methyl orange at the end of the observations and proven to be a little alkaline in reaction.

Table XI.

V.	μ_v.	Δ[1].	μ_∞.
32	73.8	12.1	85.9
32	73.8	12.1	85.9
48	75.6	10.4	86.0
64	76.4	9.6	86.0
96	78.0	7.8	85.8
128	78.8	7.0	85.8
192	80.4	5.8	86.2
256	80.5	5.2	85.7
256	81.1	5.2	86.3
		Mean,	85.96

Table XII.

V.	M_{obs}.	100 x.	$10^{-4} \times K_{hydrolysis}$.
32	79.25	2.10	7.1
48	82.83	2.77	6.1
64	84.85	3.20	6.1
96	88.84	4.12	5.4
128	91.70	4.91	5.1
192	94.73	5.45	6.1
256	99.30	7.16	4.6
		Mean,	5.8×10^4

The affinity constant[2] is then 3.7×10^{-10}.

The Affinity Constant of Ethyl Imidobenzoate Determined by a Colorimetric Method.

The determination consisted in simply taking equal volumes of water solutions of the hydrochloride of known concentration, placing them in color-comparison tubes with the same amounts of methyl orange, and adding standard acid to the water until the red tint matched the red of the salt solution employed. Knowing the volume of the water and the amount of standard acid used and the concentration of the imidoester hydrochloride, a simple calculation gave the amount of free acid formed by hydrolysis and the degree of hydrolysis. The following table, XIII., gives the results. Column one gives the volume containing a gram molecule of the salt; two, the percentage of hydrolysis; and column three, the hydrolysis constant as calculated by the equation previously used.

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[1] Bredig's differences refer to 25° C. A temperature correction of 0.019 per degree was used.

[2] K_{H_2O} was taken as 0.64×10^{-14} at 18°, according to Arrhenius: "Lehrbuch der Elektrochemie," p. 186.

Table XIII.

V.	$100x$.	$10^{-5} \times K_{hydrolysis}$.	V.	$100x$.	$10^{-5} \times K_{hydrolysis}$.
32	0.46	15	64.0	0.66	15
(32)	(0.36)	(25)	95.6	0.75	17
32	0.43	17	95.6	0.82	12
64	0.72	12	191.3	1.27	12
64	0.61	17	382.6	2.00	10

Mean, 14×10^5

Mean by conductivity, 9.1×10^5.

THE VELOCITY OF DECOMPOSITION OF THE HYDROCHLORIDES OF IMIDOBENZOATES.

In order to determine the reacting substance in the decomposition of an imidoester by water into an ester and ammonia (equation 2 or 2′), and to establish rigorously the cause of the acceleration of the decomposition by the addition of an acid, the velocity of the change of methyl imidobenzoate, in the presence of hydrochloric acid, was determined under varying conditions, at a temperature of 25° (+0°.01), and the experimental data subjected to analysis. In most of the experiments the hydrochloride of the imidoester was used alone; in other cases the experiments were carried out with an excess of the free base present with the hydrochloride. In either case, we have simultaneously two reactions taking place, with still a third reaction, according to equation (1), which is exceedingly slow and ordinarily negligible, but which was, nevertheless, taken into account, as previously described.[1] A condition of equilibrium is established between the salt, base, acid, and water according to equation (3), which is continuously disturbed by the water decomposing one of the constituents of the system into ammonium chloride and acid ester (equation 2′); the condition of equilibrium in (3) may be said to establish itself at each instant in conformity to the changing conditions, since only direct, simple ionic reactions are involved; consequently, we have at every moment, according to Walker[1] and Arrhenius,[2] for the hydrolyzed salt solution, an equilibrium according to equation (3):

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[1] Stieglitz: *Loc. cit.*

$$C_{salt} = K_{hydrolysis} \times C_{base} \times C_{acid}.$$

In the second place, the decomposition is proceeding with a measurable velocity, either the total substance, the salt and base indifferently, or only the free base or the salt (*i. e.*, its positive ions in the dilute solution used) reacting with water to give the products of the action represented in equation (2).[3]

The first possibility that the total substance, base and salt indifferently, enter into action with the water, may be taken to illustrate the principle of an acceleration produced by the acid present, an acceleration not due to the salt formation, which, of course, inevitably follows, but, in some mysterious way, to the mere presence of the acid in the system. For this case we have a monomolecular reaction proceeding with a velocity proportional to the total substance present.

$$\frac{dx}{dt} = k_{subst} \times C_{subst}. \qquad (5),^4$$

$$k_{subst} = \frac{1}{t_2 - t_1} \text{ log nat } \frac{C - x_1}{C - x_2} \qquad (6).$$

The reliability of such an interpretation is best ascertained by applying the equation to the data obtained for velocity determinations, in which an excess of free base is added to the salt solution. The degree of hydrolysis, when the salt is used alone, being exceedingly small (see $100x$ in Tables IV., VI., etc.), the total substance is almost the same as the salt content. Column seven, Table XIV., gives the values for $k_{subst.}$ calculated under these conditions according to (6), and a comparison of experiment four, in which no excess of free base was present, with experiment five, where an excess of free base was used, shows that $k_{subst.}$ is no true constant.

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[1] Z. physik. Chem., **4**, 319 (1889).

[2] *Ibid.*, **5**, 17 (1890).

[3] Stieglitz: *Loc. cit.*

[4] $C_{subst.}$ is a function of x.

The second possibility,

$$\frac{dx}{dt} = k_{base} \times C_{base},$$

that the free base present in the hydrolyzed solution is the active substance present, represents another possibility of an enhanced reactivity, not due to salt formation simply, but to some other undiscovered property of the hydrochloric acid.[1] The analysis of this case is more complicated than the previous one. Stieglitz finds for this case that we would have

$$k_{base} = \frac{1}{K_v\,(t_2 - t_1)}\Bigg[\sqrt{R - 4K^v\,x_1} - \sqrt{R - 4K_v\,x_2} + (1 - s - K_v)\log\text{ nat }\frac{\sqrt{R - 4K_v\,x_2} + (1 - s - K_v)}{\sqrt{R - 4K_v\,x_1} + (1 - s - K_v)}\Bigg] \quad (7),$$

in which $R = (1 - s + k_v)^2 + 4K_v\,s$ and the total original concentration of the imidoester used, both as salt and as free base, is called one gram molecule in V liters, the known original concentration of the salt (the added acid) s gram molecules in V liters, and x_1 and x_2, the parts of a gram molecule in V liters decomposed in t_1 and t_2 minutes, respectively. For a given experiment V is a given number and K_v is used for $V/K_{hydrolysis}$, the latter being the hydrolysis constant of equation (3) as established by Tables IV., VI., etc. When no excess of free base is used ($s = 1$), the base present in the solution results entirely from the hydrolysis of the hydrochloride and we may calculate k_{base} from

$$k_{base} = \frac{2}{(t_2 - t_1)\sqrt{K_v}}\Big[\sqrt{1 - x_1} - \sqrt{1 - x_2}\Big] \quad (8).$$[2]

A few calculations of k_{base}, made according to (7) and (8), are given in column six, Table XIV., and comparison of the values of k_{base} in experiments three and five, in which excess of free base was absent and present, respectively, shows that k_{base} is as little a true constant as k_{subst}.

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[1] See Stieglitz: This Journal, **39**, 402, in which such theories are critically considered.

[2] Stieglitz: *Loc. cit.*

In the third possibilty considered, the fact that addition of an acid accelerates the decomposition of an imidoester and at the same time forms its salt made it extremely probable, according to Stieglitz, that the reacting substance in equation (2) would be found to be rigorously the salt (the positive ions, in the dilute solutions used), in which case the reaction velocity would be accelerated simply in proportion to the increased concentration of the salt. For this case

$$\frac{dx}{dt} = k_{salt} \times C_{salt} \qquad (9)^1,$$

and we have:

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\frac{1 - s + K_v}{1 - s} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} - (1 - s + K_v)}{\sqrt{R - 4K_v x_2} - (1 - s + K_v)} + \frac{1 - s - K_v}{1 - s} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} + (1 - s - K_v)}{\sqrt{R - 4K_v x_2} + (1 - s - K_v)}\right] \qquad (10),^2$$

or, considering only the values affecting the significant numbers in the result, we have the simpler expression:

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{\sqrt{R - 4K_v x_1} - (1 - s + K_v)}{\sqrt{R - 4K_v x_2} - (1 - s + K_v)} \qquad (10'),$$

in which the symbols have the same significance as in (7). When $s = 1$, as is the case when no free base is added, we have

$$k_{salt} = \frac{1}{t_2 - t_1}\left[\log \text{nat} \frac{1 - x_1 - \sqrt{(1 - x_1) K_v}}{1 - x_2 - \sqrt{(1 - x_2) K_v}} - \sqrt{\frac{K_v}{1 - x_1}} + \sqrt{\frac{K_v}{1 - x_2}}\right] \qquad (11).$$

For less rigorous calculations, when $s = 1$, the salt being very little hydrolyzed, we may use the simple logarithmic form, for determining k_{salt}, with a sufficient degree of accuracy:

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (12).$$

The analysis of the experimental data as given in Table XIV., column five, shows that constant values for k_{salt} are obtained, regardless of the varying conditions used.

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[1] *Csalt* is a function of *x*.

[2] Stieglitz: *Loc. cit.*

Ethyl Imidobenzoate.

The results obtained for ethyl imidobenzoate at 25° are given in Table XIV. In later tables the influences of added electrolytes (excess of acid) on the velocity of the reaction will be given, as well as the reaction velocities at lower temperatures than 25°.

In column one of the table are given the conditions of the experiment, the volume V containing one gram molecule of the total substance (free base and salt), s representing the proportion of salt used, and v the volume of solution taken for each titration. Column two gives the time in minutes; three, the cubic centimeters of tenth-normal alkali neutralized by the imidoester salt (see p. 439); four gives the percentage of substance decomposed in time t. In column five is given the constant for k_{salt} as calculated by means of equation (10), or, in the absence of an excess of free base, from (11) or (12). Column six shows the values of k_{base} as calculated by means of equation (7), while column seven gives the constant for k_{subst} as calculated with common logarithms according to equation (6).

Table XIV.—Ethyl Imidobenzoate at 25°.

	t.	v.	$100x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
1.	0	11.99	5.03	...	....	....
$V = 20$	60	9.94	21.27	313	....	....
$s = 1$	120	8.26	34.58	312	....	....
	180	6.81	46.06	316	....	....
$v = 25$	620	1.64	87.00	323	....	....
		Mean:	k_{salt}	= 0.00316	....	....
2.	0	12.21	3.30	...	....	....
$V = 20$	60	10.14	19.69	310	....	....
$s = 1$	110	8.61	31.81	320	....	....
$v = 25$	300	4.85	61.59	310	....	....
		Mean:	k_{salt}	= 0.00313	....	....
3.	0	12.50	0.0	...	....	....
	5	12.18	2.56	...	....	....
$V = 20$	40	10.95	12.40	306	0.62	....
$s = 1$	80	9.71	22.32	304	0.60	....
$v = 25$	180	7.14	42.88	308	0.56	....
	300	4.96	60.32	306	0.51	...
	540	2.38	80.96	308	0.44	....
		Mean:	k_{salt}	= 0.00306		

Table XIV—(Continued).

	t.	v.	$100\,x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
4.	(10)	(9.76)	(2.40)	...	....	...
	60	8.56	14.40	(262)	....	...
$V = 10$	120	7.11	28.90	310	....	134
$s = 1$	210	5.45	45.50	304	....	131
$v = 10$	270	4.55	54.50	304	....	131
	330	3.78	62.20	306	....	132
	450	2.62	73.80	306	....	132
	570	2.08	79.20	(276)	....	...

Mean: $k_{salt} = 0.00306$

	t.	v.	$100\,x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
5.	0	12.50	0.0	...	....	..
	10	12.18	2.56	...	....	..
$V = 20$	70	10.64	14.88	287	0.0084	98
$s = 0.75$	160	8.74	30.08	299	0.0074	96
$v = 25$	250	7.26	41.92	305	0.0063	94

Mean: $k_{salt} = 0.00297$

The grand average for k_{salt} is 0.00307.

Methyl Imidobenzoate.

The following table gives the data and the constants calculated for methyl imidobenzoate. As for the ethyl ester, K_{salt} is the only real constant under all conditions.

Table XV.—Methyl Imidobenzoate at 25°.

	t.	v.	$100\,x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
1.	0	(10.05)	(20.4)	...	....	....
	60	8.76	30.62	...	....	....
$V = 20$	120	6.22	50.74	573	....	....
$s = 1$	180	4.44	64.83	568	....	....
$v = 25$	300	2.25	82.18	568	....	....

Mean: $k_{salt} = 0.00570$

	t.	v.	$100\,x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
2.	0	11.09	11.28	...	....	...
$V = 40$	40	8.51	31.92	...	....	...
$s = 1$	100	6.07	51.44	571	....	245
$v = 50$	170	4.06	67.52	577	....	247
	210	3.24	74.08	576	....	247
	270	2.31	81.52	576	....	246
	330	1.63	86.96	580	....	247
	390	1.16	90.72	580	....	248

Mean: $k_{salt} = 0.00577$

Table XV—(Continued).

	t.	v.	$100x$.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
3.	0	(12.50)	.....	...	....	....
	25	10.83	13.36	...	....	....
V = 20	65	8.67	30.64	560	....	....
s = 1	110	6.68	46.56	573	....	....
v = 25[1]	170	4.96	60.32	543	....	....
	260	3.18	74.56	530	....	....
	350	2.04	83.68	520	....	....
	440	1.18	90.56	541	....	....
		Mean: k_{salt} = 0.00545				
4.	0	(12.50)	....	...	....	...
	10	11.80	5.60	...	....	...
V = 20	40	9.89	20.88	(592)	0.771	(256)
s = 1	85	7.83	37.36	551	0.680	238
v = 25[2]	130	6.15	50.80	548	....	236
	220	3.83	69.36	541	0.560	233
	310	2.31	81.52	550	....	236
	400	1.42	88.64	550	0.430	235
		Mean: k_{salt} = 0.00548				
5.[3]	0	15.95	....	...	....	...
	5	15.38	3.57	...	....	...
V = 15.7	45	12.77	19.94	603	0.0195	202
s = 0.784	85	10.96	31.28	552	0.0165	184
v = 25	125	9.28	41.81	608	0.0151	183
	165	8.17	48.77	584	0.0129	172
		Mean: k_{salt} = 0.00587				

[1] v = 50 cc. for the seventh titration.

[2] v = 50 cc. for the sixth and seventh titrations.

[3] Taking into account the simultaneous very slow decomposition of the free base present into benzonitrile and methyl alcohol, according to the velocity constant as determined (see p. 86), we find for k_{salt} according to Stieglitz (*loc. cit.*):

t	45	85	125	165
$10^5 k_{salt}$	593	543	596	571

Mean: k_{salt} = 0.00576

Table XV—(Continued).

	t.	v.	100 x.	$10^5 k_{salt}$.	k_{base}.	$43430 k_{subst}$.
6[1].	0	12.50	...	...	....	...
	20	11.10	11.20	...	....	...
	60	9.35	25.20	540	0.0201	186
$V = 20$	115	7.49	40.08	568	0.0160	180
$s = 0.8$	205	5.40	56.08	568	....	170
$v = 25$	255	4.60	63.20	603	0.0707	162
	310	3.86	69.12	548	....	157

Mean: $k_{salt} = 0.00565$

Grand average: $k_{salt} = 0.00562$.

n-Propyl Imidobenzoate.

The next table gives the data for *n*-propyl imidobenzoate hydrochloride as determined and calculated for a temperature of 25°. The columns have the same significance as in the tables for the other esters.

Table XVI.—n-Propyl Imidobenzoate at 25°.

	t.	v.	100 x.	$10^5 k_{salt}$.
	0	11.98	...	...
$V = 20$	20	11.21	5.73	297
	80	9.40	20.95	295
$s = 1$	140	7.89	33.64	294
	200	6.59	44.74	304
$v = 25$	260	5.59	52.99	292
	325	4.57	61.57	295
	380	3.88	67.37	290

Mean: $k_{salt} = 0.00295$

Methyl Metanitroimidobenzoate.

The next table gives the data for the decomposition velocity of methyl metanitroimidobenzoate and shows the constants obtained. Owing to the very rapid rate of change of this substance, accurate measurements at 25° were impossible and the experiments were therefore conducted at 18°.

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[1] Allowing, as in (3), for the slow decomposition of the base, we have:

t	60	115	205	255
$10^5 k_{salt}$	540	558	571	580

Mean: $k_{salt} = 0.00562$

Table XVII.—Methyl Metanitroimidobenzoate at 18°.

	t.	v.	100 x.	$10^4 k_{salt}$.	k_{base}.	4343 $k_{subst.}$
1.	0	10.43	0.0	...	...	...
	11	7.91	24.14	256	...	109
	23	5.87	43.72	255	...	109
V = 20	35	4.33	58.47	257	...	109
s = 1	48	3.22	69.12	252	...	106
v = 25	63	2.28	78.14	249	...	105
	76	1.71	83.60	247	...	103
	88	1.27	87.82	248	...	104
	101	0.95	90.89	246	...	103
		Mean: k_{salt} = 0.0251				
2.	0	.....	.....	...	...	...
	6	10.71	13.02	...	...	...
V=18.2	17	7.99	32.80	258	0.194	102
s= 0.909	28	6.04	46.98	255	...	98
v=25	39	4.52	58.04	256	0.146	96
	51	3.31	66.84	257	...	93
	62	2.51	72.65	255	...	90
	73	1.85	77.45	259	0.104	87
		Mean: k_{salt} = 0.0257				
3.	0	10.78	0.0	...	...	...
V=40	14	7.58	29.69	251	...	109
s= 1	27	5.54	48.61	254	...	107
v=50	40	4.14	61.59	248	...	104
	52	2.95	72.64	258	...	108
	66	2.18	79.78	245	...	105
	78	1.66	80.61	(219)	...	104
	97	1.28	88.12	(230)	...	102
	103	0.95	90.10	(236)	...	103
			Mean: k_{salt} = 0.0251			

The Effect of an Excess of Hydrochloric Acid on the Velocity of Decomposition of the Imidobenzoate Esters.

The velocity of decomposition of the hydrochloride of methyl imidobenzoate into ammonium chloride and methyl benzoate was determined at 25° in the presence of excess of hydrochloric acid varying in amount from 0.05 to 0.5 mole, the salt solution being 0.05 molar. The experimental results are given below, and the conclusions based upon them follow the table. The velocity constant was calculated according to equation (12).

Table XVIII.—Methyl Imidobenzoate.

t.	v.	43430k.	t.	v.	43430k.
1. 0.05 salt, 0 acid.			2. 0.05 salt, 0 acid.		
0	11.80	....	0	10.83	...
30	9.89	(256)	40	8.68	240
75	7.83	237	85	6.68	(247)
120	6.15	236	145	4.96	234
210	3.83	233	235	3.18	227
300	2.31	236	325	2.04	(223)
390	1.42	235	415	1.18	232
	Mean,	235		Mean,	234
3. 0.05 salt, 0.05 acid.			4. 0.05 salt, 0.05 acid.		
0	12.19	...	0	10.79	...
40	9.78	239	40	8.88	(212)
80	7.81	241	85	6.82	235
120	6.26	241	120	5.64	236
220	3.81	230	185	4.00	233
	Mean,	238		Mean,	235
5. 0.05 salt, 0.10 acid.			6. 0.05 salt, 0.10 acid.		
0	12.00	...	0	(10.36)	...
40	9.95	(203)	40	8.82	...
80	8.00	220	120	5.73	234
120	6.28	234	180	4.21	229
160	5.25	224	260	2.97	215
240	3.56	220	340	1.81	229
320	2.48	214	420	1.16	232
	Mean,	222		Mean,	228
7. 0.05 salt, 0.15 acid.			8. 0.05 salt, 0.50 acid.		
0	11.53	...	0	11.15	...
35	9.50	(240)	40	9.35	191
75	8.18	199	80	7.86	190
115	6.70	205	120	6.47	197
155	5.33	216	160	5.55	189
235	3.70	210	240	3.88	191
315	2.24	226	300	3.01	190
395	1.56	220	360	2.47	182
	Mean,	213		Mean,	190
9. 0.05 salt, 0.50 acid.					
0	11.88	...			
35	10.27	181			
75	8.45	197			
115	6.98	201			
155	6.04	190			
195	4.97	194			
	Mean,	193			

Table XIX.—Ethyl Imidobenzoate.

t.	v.	$10^5 k_{salt}$.	t.	v.	$10^5 k_{salt}$.
1. 0.05 salt, 0 acid.			2. 0.10 salt, 0.10 acid.		
0	12.19	...	0	8.56	...
35	11.12	(262)	60	7.11	309
75	9.75	298	150	5.45	301
175	7.16	305	210	4.55	301
295	4.95	305	270	3.78	303
535	2.38	305	290	2.62	303
	Mean,	303		Mean,	303
3. 0.05 salt, 1 acid.			...	...	...
0	11.91	...	...	...	...
45	10.84	209	...	...	...
105	9.67	198	...	...	...
185	8.19	202	...	...	...
295	6.55	203	...	...	...
405	5.17	206	...	...	...
	Mean,	204			

According to the theory of Stieglitz,[1] the decomposition of imidoesters by water is caused by the action of the ions of water on the positive ions of the imidoester, according to

$$\mathrm{RC}(:\overset{+}{\mathrm{N}}\mathrm{H}_2)\mathrm{OR} + \mathrm{HOH} \rightarrow \mathrm{RCO_2R} + \overset{+}{\mathrm{N}}\mathrm{H}_4 \qquad (13).$$

Now, in the first place, an addition of an excess of hydrochloric acid must produce a depression of the degree of ionization of the imidoester salt, the salt ionizing in a mixture of electrolytes according to the concentration of the total electrolyte present. On the basis of the principle of isohydric solutions that solutions containing a positive or negative ion in common in the same concentration do not affect each other's ionization, one can imagine, with Arrhenius, for each of the above mixtures, the solvent so divided between the salt and the acid that solutions of like concentration of chlorine ions result, and the degree of ionization of the salt and acid in the resulting mixture may be calculated. For these calculations Schlesinger's[2] data on the degrees of ionization of the hydrochloride of methyl imidobenzoate were used, and allowance was made for the greater degree of ionization of the hydrochloric acid, which results in the acid receiving a larger share of the water than would correspond to the molecular proportions. Table XX., page 469, gives in column one the excess of acid actually used and in column two the molecular concentration of the salt, *whose degree of ionization in pure aqueous solution would correspond to that of the salt in the mixture.* Column three gives the degree of ionization of the salt corresponding to these concentrations, and column four, the degree of ionization of the acid for the mixture. The interpolations necessary were made rectilinearly from the experimental values for the nearest molecular concentrations. It was not considered important to make more exact interpolations in this series, since the relations are being more rigorously investigated in this laboratory.[1] Column five shows the mean observed velocity constants, referred to the total salt, as obtained from Table XVIII., and column six gives the velocity constant referred only to the positive ion of the salt, k_{salt} being divided by α_{salt}.

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[1] *Loc. cit.*

[2] See a later report by Schlesinger in THIS JOURNAL.

In the second place, the addition of an excess of hydrochloric acid will have a so-called "salt-effect" on the decomposition of the imidoester salt by water,[2] as it has in other changes in which water acts, such as the catalysis of esters or of cane-sugars,[3] the "salt-effect" probably consisting, in this case, in an increase of the degree of the ionization of water, that is, it probably affects the concentrations of the reacting ions of water in the reaction expressed by equation (13). This "salt-effect" is most likely produced only by the ionized portion of the acids and salts, as suggested by Arrhenius, and as results obtained in this laboratory uniformly confirm. In the experiments under consideration, after allowing for the effect of the change of the degree of ionization of the imidoester salt, it will be noted (Table XX., column 6) that 43430 k/α rises from 275 for the 0.05 salt, without any excess of acid, to 400 for an excess of 0.5 mole of acid—that is, the accelerating salt effect of 0.5 mole of acid is $\frac{400-275}{275}$ or 46 per cent. As the degree of ionization of 0.5 normal hydrochloric acid is 84.3 per cent, the acceleration per gram equivalent of *ionized* acid is 109 per cent. It is a most striking fact that for the same excess of acid in the case of ethyl imidobenzoate, whose velocity constant is only half as great as that of the methyl ester, McCracken[1] found an accelerating effect of 107 per cent, and for ethyl metanitroimidobenzoate, the velocity constant of which is five times greater than the methyl ester constant, the observed accelerating effect was 110 per cent per gram equivalent of ionized acid. This remarkable agreement, thus showing these values to be independent of the velocity constants themselves, seems to confirm the view of this reaction adopted here[2] and justifies the following calculation of what the velocity constant should be[3] in each experiment given in Table XIX. We have:

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[1] *Vide* a later article by E. E. Barnard.

[2] Stieglitz: This Journal, **39**, 166.

[3] Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889). Euler: *Ibid.*, **36**, 419 (1901).

$$K_{calc} = 262 \times \alpha_{salt} \times (1 + m_{salt} \times \alpha_{salt} + 1.09\ m_{acid} \times \alpha_{acid}) \quad (14).$$

In the equation, 262 represents the hypothetical velocity constant of decomposition of the methyl imidobenzoate in a solution of zero concentration, that is, completely ionized and free from any salt effect whatever, including the autosalt effect as developed by Schlesinger.[4]

The factor α_{salt} in the above equation makes the velocity of decomposition proportionate only to the concentration of the positive ion of the imidoester salt. The expression in the brackets gives the acceleration due to the effect in the solution of water produced, first, by the ions of the salt and, secondly, by the ions of the hydrochloric acid. The acceleration produced by the salt itself, according to Schlesinger's results, as above mentioned, is just about 100 per cent per mole of ionized salt, and the effect of m_{salt} moles[5] of salt, ionized to the extent of α_{salt} per cent, would be $m_{salt} \times \alpha_{salt}$. The average acceleration per 0.5 mole acid, dissociated to the extent of 84.3 per cent (in the mixed solutions), is 46 per cent, giving 1.09 as the acceleration per mole ionized acid. The acceleration due to m_{acid} mole of acid present is therefore $1.09 \times m_{acid} \times \alpha_{acid}$.

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[1] *Vide* a later paper by McCracken in This Journal, and Stieglitz: This Journal, **39**, 166.

[2] Stieglitz: This Journal, **39**, 166.

[3] Stieglitz: *Loc. cit.*

[4] *Vide* a later article in This Journal by H. I. Schlesinger.

[5] The real concentrations, m_{salt}, are found in Table XVIII. The values m'_{salt}, in Table XX. represent the ideal concentrations of an isohydric solution.

The last column in Table XX. gives the values of the velocity constant as calculated according to equation (14) and represents what the observed constants should be in each experiment if the velocity of the reaction in the equation (2′) is really a function only of the positive ion of the imidoester and of the ionization of water—the latter being considered dependent, in turn, on the total concentration of salt and acid ions present in the mixture. A comparison of the values in the last column with the actually observed constants (k_{obs}, column 5) shows, in fact, a most satisfactory agreement.

Table XX.

1 m_{acid}.	2 m'_{salt}.	3 $100\alpha_{salt}$.	4 $100\alpha_{acid}$.	5 43430 × $k_{obs.}$	6 $\frac{43430\, k_{obs.}}{\alpha_{salt}}$	7 43430 × $k_{calc.}$
0.0	0.0	100 0	....	...	(262)[1]	...
0.0	0.05	85.5	....	235	275	234
0.0	0.05	....	....	234	...	234
0.05	0.106	79.8	91.6	238	296	228
0.05	0.106	....	....	235	...	228
0.10	0.170	74.8	90.0	222	301	223
0.10	0.170	....	....	228	...	223
0.15	0.238	70.6	89.2	213	302	218
0.50	0.80	48.0	84.3	190	400	187
0.50	....	....	....	193	...	187

The Effect of Temperature on the Velocity Constants.

The velocity constants of the first four esters, except *n*-propyl, investigated were also determined at 18°, and in the cases of ethyl and methyl esters the reactions were followed at 0° as well. In the following table the columns and symbols have the same significance as in Table XIV. In all cases the hydrochlorides of the esters were used alone.

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[1] Hypothetical, see Schlesinger: *Loc. cit.*

Table XXI.—Ethyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$.
T = 18°	0	12.31	...	...
	50	11.46	6.89	143
	190	9.52	22.66	135
$V = 20$	280	8.42	31.59	136
$s = 1$	370	7.45	39.47	136
$v = 25$	462	6.62	46.21	135
	580	5.55	59.91	137
	1360	1.90	84.56	137
			Mean: k_{salt}	= 0.00136
$T = 0°$	0	12.44	...	....
	180	12.10	2.73	15.4
$V = 20$	480	11.57	6.99	15.1
$s = 1$	1230	10.43	16.17	14.3
$v = 25$	2670	8.43	32.24	14.6
	4210	6.82	45.17	14.3
	5620	5.46	56.11	14.7
			Mean: k_{salt}	= 0.000147

Summarizing the results given in Tables XIV. and XXI., we have as the effect of temperature on the velocity constant:[1]

T	0°	18°	25°
$10^5 k_{salt}$	15.4	136	307
Veloc. ratio	0.0502	0.433	1

Methyl Imidobenzoate.

	t.	v_t.	100 x.	$10^5 k_{salt}$
1.	0	11.08	...	...
$T = 18°$	45	9.99	9.82	(230)
$V = 20$	105	8.60	22.38	241
$s = 1$	195	6.82	38.44	249
$v = 25$	285	5.43	50.99	250
	375	4.35	60.74	249
	495	3.28	70.40	246
			Mean: k_{salt}	= 0.00247
2.	0	11.01	0.0	....
$T = 0°$	90	10.68	3.00	33.8
$V = 20$	390	9.70	11.90	32.5
$s = 1$	1165	7.92	28.06	28.3
$v = 25$	1705	6.88	37.50	27.4
	2605	5.21	52.68	28.8
	4045	3.61	67.21	27.4
			Mean: k_{salt}	= 0.000297

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[1] The theoretical discussion of this effect is reserved for a later paper.—J. Stieglitz.

The effect of temperature change on the velocity constant is shown by the summary of Tables XV. and XXI.:

T	0°	18°	25°
$10^5 k_{salt}$	29.7	247	562
Veloc. ratio	0.0529	0.440	1

Isopropyl Imidobenzoate.

	$t.$	$v_t.$	$100\,x.$	$10^5 k_{salt}.$
I.	0	12.27	0.0	....
$T=18°$	410	10.20	16.88	45.6
$V=20$	1320	6.86	44.10	44.1
$s = 1$	1820	5.37	56.24	45.4
$v = 25$	2800	3.45	71.89	45.3
	3380	2.72	77.84	44.6
	4250	1.88	84.65	44.1

Mean: $k_{salt} = 0.000448$

The values of the velocity constants from Table XVII. and XXI. are:

T	18°	25°
$10^5 k_{salt}$	44.8	103
Velocity ratio	0.435	1

THE VELOCITY OF REACTION OF THE FREE IMIDOESTERS IN AQUEOUS SOLUTIONS.[1]

Attention has been called to the fact that free imidoesters alone in water solution decompose very slowly, according to

$$\text{RC(:NH)OR} \rightarrow \text{RCN} + \text{ROH} \qquad (1),^{2}$$

and since this change is simultaneous with the main reaction of the ionized salt (the free base formed being due to hydrolytic dissociation), it was necessary to determine the velocity constant in order to correct the observed velocity constants and thus determine the true constant of the salt.[3] The two products of decomposition of the free esters are neutral substances, so that the course of the reaction could be followed simply by direct titration, from time to time, of measured volumes of solution with standard acid and methyl orange, taking, of course, the precautions regarding the end tint described under the analyses of the free esters. The reaction is a monomolecular one, proceeding according to

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[1] See the detailed discussion of this reaction in Stieglitz's paper: THIS JOURNAL, 39, 166.

[2] A nitrile is the main product. Probably a small amount of benzamide is also formed.

[3] A few calculations in which this correction has been applied are given in the footnote on page 462. It was found to be trifling.

$$\frac{dx}{dt} = k_{ester} \times (C_{ester} - x),$$

and

$$k_{ester} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2}.$$

The following table shows the results obtained for the various esters at 18° and 25°. The columns and symbols have the same significance as in previous tables. Owing to the slight solubilities of these esters, dilute solutions were necessarily used:

Table XXII.—Ethyl Imidobenzoic Ester.

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
1.	0	3.65	...	...
$T=18°$	1240	3.10	15.1	13.2
$V=60$	2140	2.74	24.9	13.4
$v=25$	3560	2.25	38.4	13.6
		Mean: k_{ester}	=	0.000134
2.	0	6.19	0.	...
	350	5.63	9.10	27.1
$T=25°$	1110	4.57	26.2	27.3
$V=40$	1580	4.01	35.2	27.5
$v=25$	2480	3.04	50.9	28.7
	3220	2.43	60.7	29.0
	3940	1.98	68.0	28.9
	5380	1.38	77.7	27.9
	6800	0.96	84.5	27.4
		Mean: k_{ester}	=	0.0002797

Methyl Imidobenzoic Ester.

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
1.	0	3.23	0.	...
	1790	2.57	20.4	12.8
$T=18°$	2720	2.25	30.3	13.3
$V=31$	4120	1.91	40.9	12.8
$v=10$	5560	1.56	51.7	13.4
	7000	1.34	58.5	12.6
		Mean: k_{ester}	=	0.000130

Table XXII—(Continued).

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
2.	0	12.49	0.0	...
$T = 25^\circ$	200	11.85	5.05	25.9
$V = 20$	400	11.28	9.62	25.3
$v = 25$	1340	8.66	30.6	27.3
	2750	5.72	54.2	28.4
	4200	3.75	70.0	28.6

Mean: $k_{ester} = 0.000271$

Isopropyl Imidobenzoic Ester.

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
1.	0	1.513	0.0	...
$T = 18^\circ$	2340	1.319	12.8	5.85
$V = 150$	3750	1.247	17.7	5.16
$v = 25$	5180	1.141	24.6	5.45
	6600	1.054	30.3	5.48
	8070	0.962	36.4	5.61
	13890	0.696	54.0	5.59

Mean: $k_{ester} = 0.0000552$

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
2.	0	2.012	0.0	...
	490	1.938	(3.66)	(7.6)
$T = 25^\circ$	1230	1.702	15.42	13.6
$V = 125$	1790	1.600	20.5	12.8
$v = 25$	2670	1.438	28.5	9.9
	4100	1.180	41.3	13.0
	5560	0.962	52.3	13.3
	7020	0.818	59.3	12.8

Mean: $k_{ester} = 0.000126$

Methyl Metanitroimidobenzoic Ester.

	t.	v_t.	$100\,x$.	$10^5 k_{ester}$.
1.	0	2.40	0.0	...
$T = 18^\circ$	420	2.27	7.58	(18.70)
$V = 208$	1400	2.17	9.58	9.19
$v = 50$	2730	1.95	18.76	7.69
	4170	1.74	27.5	7.71

Mean: $k_{ester} = 0.000075$

It is evident that, in every instance, good constants are obtained for a reaction proceeding with a velocity proportionate to the total concentration of the ester.

It is with pleasure that I acknowledge the painstaking care with which Professor Stieglitz directed and followed my work, and I wish to express to him my appreciation and deep gratitude for all he has helped me to accomplish.

CHICAGO, September, 1907.

THE INFLUENCE OF RADIUM ON THE DECOMPOSITION OF HYDRIODIC ACID.

By H. Jermain M. Creighton and A. Stanley Mackenzie.[1]

The first mention of the influence of radiant energy of any kind on chemical reactions was made by William Cruickshanks,[2] who observed that hydrogen and chlorine combine under the influence of light. This particular reaction has been the source of many investigations, carried out by such men as Dalton,[3] Draper,[4] Bunsen and Roscoe, and, more recently, Mellor,[5] Bevan,[6] and Burgess and Chapman.[7] Of the numerous reactions affected by light the following are some of the more important: Influence of light on silver salts, on the action of bromine and chlorine on metallic silver, on dyed colors, on enzymes in oxygen and hydrogen, on glass, on the oxidation of iodoform, on the action of oxygen on carbon bisulphide, on the decomposition of hydrogen peroxide, on the combination of hydrogen and bromine, on the reaction between chlorine and benzene.

Other forms of radiant energy whose effects on chemical action have been investigated are ultraviolet light, Röntgen rays, and radium radiations.

Only a comparatively small amount of work has been carried out on the effect of radium on chemical reactions. Hardy and Wilcocks[8] have investigated the oxidation of iodoform when acted on by Röntgen rays and by radium, and Hardy[9] has observed the coagulation of globulin under the influence of the latter rays. Becquerel[10] found that white phosphorus is changed into the inactive red phosphorus and that mercuric chloride, in the presence of oxalic acid, is reduced to mercurous chloride by the radiations from radium. The Curies[1] have shown that the rays from radium change oxygen into ozone, and discolor glass. Berthelot[2] cites the following cases: Iodic acid is decomposed by radium rays and by light, with liberation of iodine, this change being much slower than that of iodoform; nitric acid gives off nitrous fumes when acted on by radium and by light. These reactions appear to be all that have been investigated up to the present time.

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[1] In this paper an investigation already published by one of us is developed and enlarged (Creighton: P. and Trans. Nova Scotia Inst. of Sc., **12**, p. 1).

[2] Nicholson's J. [1], **5**, 202 (1801).

[3] A New System of Chem. Phil., p. 300.

[4] Phil. Mag. [3], **25**, 9 (1844); **26**, 473 (1845).

[5] J. Chem. Soc., **86**, 53 (1904).

[6] P. Camb. Phil. Soc., **2**, 264–266 (1902).

[7] J. Chem. Soc., **88**, 1399 (1906).

[8] P. Roy. Soc., **72**, 200, 480.

[9] P. Phys. Soc., May 16, 1903.

[10] Compt. rend., **133**, 709 (1901).

These investigations have been mainly of a qualitative nature, the quantitative side receiving very little attention. The following experiments were carried out with a view to finding out whether a quantitative examination of the change, if any, produced in hydriodic acid by the presence of radium would throw light on the part played by the rays in this decomposition. Hydriodic acid was chosen on account of its instability, and from its behavior under the influence of light it was believed that it would be affected by radium rays.

The effect of light on the decomposition of hydriodic acid has been largely investigated in the last few years. Pinnow,[3] who has done a large amount of work on this subject, used acid solutions of potassium iodide for the production of the hydriodic acid. He found that the best results were obtained when the solution of potassium iodide used had a concentration of one gram per liter. It was a solution of this strength that was used in all the following work. The hydriodic acid was set free from the iodide by a solution of sulphuric acid consisting of one part of acid (sp. gr. 1.84) to five parts of water. The proportion of acid to iodide solution was one to eight.

The amount of oxidation was determined, in the usual way, by titrating the liberated iodine with 1/1250 normal sodium thiosulphate solution.

It was found that the end point could be determined very quickly and accurately by highly illuminating the solution by means of an electric light placed behind it and reflecting back the rays through the solution by placing a piece of white paper around the beaker on the opposite side.

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[1] Compt. rend., **129**, 823 (1899).

[2] *Ibid.*, **133**, 659 (1901).

[3] Ber. d. chem. Ges., **34**, 2528 (1901).

The potassium iodide used was the chemically pure, guaranteed reagent supplied by C. F. Kahlbaum.

By carrying out the titration in the above manner the error was found to be about ±0.08 cc. sodium thiosulphate solution.

Five milligrams of radium bromide, of activity of about 1,000,000, were employed. The radium was enclosed in a small glass tube, so that only the β- and γ-rays were used.

The starting point in the investigation was to determine whether radium exerted any influence on the oxidation of hydriodic acid. For this purpose the radium was placed over a vessel containing the acid solution of potassium iodide, of the concentration mentioned above, and its rays allowed to bombard the solution for a certain time; at the end of that time the amount of decomposition was compared with that of a similar solution which had not been acted upon by radium. The vessels used to contain the solutions were ordinary wide-mouthed reagent bottles, with a capacity of about 125 cc. The small glass tube containing the radium was held in the end of a hollow brass rod which was placed in a fixed position in a wooden block; this latter fitted into the mouth of one of the bottles. Thus, by filling the bottle to a definite mark, the distance between the radium and the surface of the liquid was always kept the same. The distance was between two and three millimeters.

These experiments were all carried out in a photographic dark room, so that there was no chance of the reaction being influenced by light. The solution which was not to be acted upon by radium was protected from the rays by a screen of lead, so placed that the solution would not be affected appreciably by the secondary rays set up in the lead.

Several experiments carried out in this way showed, at the end of twenty-four hours, that the decomposition in the solution acted upon by radium was greater than the decomposition in the other; but the excess varied in different trials from 15 per cent to 25 per cent. In order to obtain more concordant results for similar experiments the temperature at which the reaction took place was kept constant for a series of measurements, and it was found that this made a decided improvement in the agreement of the results. It was still found, however, that the differences in results under similar conditions were considerably greater than those due to experimental error. In order to see whether these differences were due to small errors in the mixing of the solutions, a large quantity of solution was prepared and divided into six equal parts of 225 cc. each. These were allowed to stand for twenty hours in a dark room, without radium, at a temperature of 16° ± 0°.5 C. At the end of that time the amount of decomposition, as measured by the number of cc. of titrating solution required, was found to be, for the several portions, 5.38, 5.23, 5.41, 5.34, 5.07, 5.33, respectively. The lack of equality of these numbers shows that the irregularity is not to be accounted for in this way.

The influence of the impurities in the ordinary distilled water used in making up the solutions was next investigated, and it was found that when the water had a conductivity, expressed in Kohlrausch's unit,[1] (ohm^{-1} cm.^{-1}), of 2.0×10^{-6}, or less, at 18° C., the agreement between the amounts of decomposition of several similar solutions was within the limit of experimental error.

The water used in the following experiments was prepared according to the method of Jones and Mackay.[2] The ordinary distilled water was doubly distilled. The steam from the first flask, which contained the water mixed with an alkaline solution of potassium permanganate, was bubbled through an acid solution of potassium bichromate in a second flask. Into the neck of the latter was thrust a block-tin condenser, which was held there by means of a cork made of a mixture of plaster of Paris and asbestos. The water thus obtained had a mean conductivity of 1.6×10^{-6} at 18° C. It was kept in bottles which had been used several years for that purpose.

It was found that the purity of the water, as determined by its conductivity, played an important part in the rate of decomposition of the solution. The table below shows the results obtained when using water of two different grades of purity in the preparation of the solutions.

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[1] Kohlrausch und Holborn: "Leitvermögen der Elektrolyte," 1898, p. 1.

[2] Z. physik. Chem., **22**, 237 (1897).

In this table, and those that follow, the numbers given denote the amount of 1/1250 normal sodium thiosulphate solution required to titrate the free iodine content in the hydriodic acid solution at the times specified after the instant of mixing. The mixing was done in the dark room. In all cases the amount of hydriodic acid solution experimented upon was 50 cc.

The numbers in the following table are for the case where the mixture was left to stand in the dark room, and was not subjected to the action of radium or any other external action. The temperature was 15° ± 0°.5 C.

Table I.

Time in hours.	No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when hydriodic acid solutions were made up with water of	
	conductivity 4.98×10^{-6}.	conductivity 2.16×10^{-6}.
7	0.73	0.90
11	0.97	1.04
15	1.38	1.40
20	1.68	1.63
25	2.05	....
30	2.45	1.79
35	2.80	....
40	2.86	1.95
50	3.20	....
70	4.05	....
95	4.37	3.08
120	4.25	3.35
170	3.75	3.24
200	3.24	3.24
300	3.45	3.22
380	1.58	3.23
450	....	3.21
550	....	3.25
650	0.89	3.20
1100	....	3.24

From an examination of this table it will be seen that there is a striking difference between the behavior of solutions made up with ordinary distilled water and of those made up with water which had been more carefully purified. For the less pure water the content of free iodine rose to a maximum in about four days, and then gradually fell off again; but with the purer water the iodine content increased with the time for the first five days, and then remained constant for the next six weeks during which it was under observation. Similar hydriodic acid solutions made up with the less pure water were subjected to sunlight, and in that case also the amount of iodine increased at first, reached a maximum after some days, and finally disappeared entirely. Hence the effect of impurity in the water is of the same nature whether the solution be left in the dark or acted on by sunlight. It will be seen later that in certain circumstances radium has the same effect on solutions made up with the purer water.

It would seem that the effect of the small amount of impurity in the water is to cause the formation, by some sort of catalytic action, of a third iodine product in addition to the hydriodic acid and free iodine which alone we might at first sight expect. In the case of solutions made up with the purer water, where the iodine content tends towards a constant asymptotic value, as given in the third column of the above table, the simplest explanation is that the third product is not being formed, and that we have there the ordinary equilibrium between the hydriodic acid, the hydrogen, and the iodine. If the third product is still being formed, two suggestions present themselves to account for the continued constancy of the amount of free iodine present: (1) that the rate of formation of the third product is very small, but that in time the numbers in the last column of the table would begin to decrease also; (2) that the whole system reaches a state of equilibrium, and the iodine content will be constant however long the time. The former suggestion is the more probable one, since it is likely that even by the more careful distillation of the water we have not entirely got rid of the cause of the trouble but only reduced it in amount.

This, however, is not the only effect of the impurity in the water; it also accelerates the rate of accumulation of iodine.

This is evident from the fact that the maximum value reached in the case of the less pure water is greater than the asymptotic value approached in the case of the purer sample. As it was found that the rate of production of free iodine was much affected by the temperature, it was felt that an answer to the question of whether radium radiations had a specific action of their own on hydriodic acid or only changed in degree the action going on in their absence was to be looked for from a study of the action at different temperatures both in the presence and in the absence of radium. Further efforts at an explanation of the action of external agencies, such as impurity, light, Becquerel rays, etc., will therefore be deferred until the experiments on the effect of temperature on solutions with and without radium have been detailed.

The following table contains the results obtained with water of a high degree of purity, at a temperature of 24° C., both with and without radium. A new sample of 50 cc. of hydriodic acid solution was taken for each period of time shown.

Table II.

	No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of			
	no radium		radium	
Time in hours.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 1.54$, $b = 0.175$.	observed.	calculated from $y = a(1-e^{-bt})$; $a = 2.10$, $b = 0.175$.
2	0.45	0.45	0.58	0.62
3	0.65	0.63	0.85	0.86
5	0.92	0.90	1.25	1.23
7	1.10	1.09	1.51	1.48
10	1.23	1.27	1.73	1.73
12	1.27	1.35	1.77	1.85
16	1.38	1.45	1.94	1.98
21	1.52	1.50	2.10	2.05
38	1.56	1.54	2.09	2.10

In the third and fifth columns of the table are added numbers calculated from the equation

$$y = a(1 - e^{-bt}) \qquad (1),$$

with the values of a and b there given, to show how well the observations are represented by curves of this type. These calculated curves are plotted as N(24°) and R(24°) in Fig. I., the amounts of sodium thiosulphate solution being represented as ordinates, and the times as abscissas. The observed values are marked, and lie remarkably well on the curves.

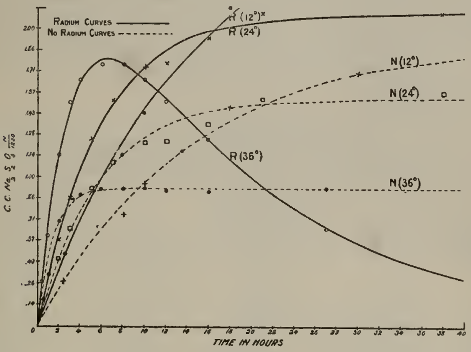

Fig. I.

The similarity of the two curves seems to show that with pure water, at this temperature, the action of the radium is of the same nature as that which goes on without it in the dark, but is greater.

The reaction was next observed at 12° C., and a few readings made to determine the behavior at that temperature. The results are given in the following table:

Table III.

No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of

Time in hours.	no radium		radium	
	observed.	calculated from $y = a(1 - e^{-bt})$; $a = 1.92$, $b = 0.07$.	observed.	calculated from $y = a(1 - e^{-bt})$; $a = 2.90$, $b = 0.07$.
2.5	0.30	0.31	0.49	0.46
8	0.75	0.83	1.15	1.25
10	0.95	0.96	1.43	1.46
18	1.47	1.37	2.15	2.08
30	1.69	1.69	2.55	2.55

The curves for this case are those marked N(12°) and R(12°) in Fig. I. The only difference between the behavior at this temperature and that at 24° is that at the former the decomposition of the solution is much slower, and the equilibrium values are consequently greater and longer in being reached. The effect of the radium is again, apparently, only to increase the action in degree but not to change it in type.

The next experiments were made at 36°, and the results are shown in Table IV.:

Table IV.

No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of

	no radium		radium	
Time in hours.	observed.	calculated from $y = a(1 - e^{-bt})$; $a = 0.92$, $b = 0.70$.	observed.	calculated from $y = a(e^{-bt} - e^{-ct})$; $a = 3.3$, $b = 0.06$, $c = 0.31$.
0.5	0.18	0.27	0.30	0.38
1	0.35	0.46	0.60	0.69
2	0.70	0.69	1.15	1.15
3	0.85	0.81	1.50	1.46
4	0.88	0.87	1.65	1.64
6	0.93	0.91	1.75	1.79
8	0.92	0.92	1.75	1.75
10	0.93	0.92	1.65	1.64
12	0.91	0.92	1.50	1.52
16	0.90	0.92	1.25	1.24
27	0.93	0.92	0.65	0.65

The curves for this case are marked N(36°) and R(36°) in Fig. I. It will be seen that the curve for no radium, N(36°), is still of the same logarithmic form as the curves for no radium and radium at both 12° and 24°. A comparison of the no radium curves for 12°, 24°, and 36° shows that as the temperature increases the times taken to reach the equilibrium value decrease, being approximately 60, 23 and 6 hours, respectively; and the equilibrium values correspondingly decrease, being 1.92, 1.54, and 0.92, respectively. This denotes an increased rate of formation of free iodine as the temperature is increased. The same thing is true of the radium curves for 12° and 24°. The radium curve for 36°, R(36°), however, is of an entirely different form from these five; it rises steeply toward a maximum, and then steadily falls off again. It has exactly the same form as the curve for impure water with no radium, which we considered earlier. It is most probable that this is more than a coincidence, and it is reasonable to suppose that what the impurity does at the lower temperature the radium also does at this higher temperature.

The form of the curve R(36°) suggests an equation of the type

$$y = a(e^{-bt} - e^{-ct}) \qquad (2).$$

It is well known that for this equation the latter part of the downward slope of the curve is practically determined by the smaller of the two quantities b and c. Accordingly, from the observed values of y at 12, 16, and 27 hours, b was found to be 0.06 and a to be 3.3. The value of c can be found from the fact that at the maximum, calling the time at this instant T hours, we have the relation

$$be^{-bT} = ce^{-cT}.$$

Putting for T the value 6.6, found from the curve, and for b its value 0.06, we find c to be 0.31. The numbers calculated from equation (2) with these values of the constants are given in the last column of Table IV., and the agreement with the observed values falls well within the limit of error.

It is now necessary to frame an hypothesis of what is going on which will be consistent with the known properties of the chemical substances used, and with the behavior observed experimentally.

The reaction between H_2SO_4 and KI is presumably a bimolecular, reversible one, and since the solution, as mixed, contains 65 equivalents of acid to 1 of iodide, we would be inclined to suppose that the equilibrium value of HI is nearly equal to the amount of KI used, and is reached in a comparatively short time. If we knew the values of the direct and reverse rates of the reversible reaction this could be quickly tested, but these constants we have been unable to find. Differential equations were formed after the manner of those given below and solved on the supposition that the HI is formed slowly from the KI, but this supposition failed entirely to fit in with all the experimental results. Accordingly, in what follows the HI, as a first approximation, is assumed to be formed instantaneously and to the maximum amount. This latter amount is 336, when expressed in cc. of N/1250 sodium thiosulphate solution, the unit in which all our observed numbers are expressed. This assumption does not seem to be in accord with the observations of Pinnow,[1] who found that the amounts of thiosulphate required in titration were proportional to the number of equivalents of acid used with one equivalent of iodide, but it is to be remembered that he was measuring the content of free iodine, not of HI. His results could be made to accord with our assumption if we suppose that the sulphuric acid stimulated the change of HI into free iodine.

Perhaps the most obvious supposition to make in order to account for the decrease of free iodine after 7 hours, when the reaction takes place at 36° under the influence of radium, is that the iodine is being transformed into a third product. We can easily find an equation for the amount of free iodine at any time, in this case, if we consider that the reactions which take place are monomolecular. Call n the total initial amount of HI, and x the amount at any time t. Call y the amount of free iodine at that time. Let k_1 and k_2 be the direct and the reverse velocity constants in the reversible reaction $HI \rightleftarrows H + I$, and λ the similar quantity in the conversion of the iodine into a third product. We have to solve the equations

$$\left.\begin{aligned} \frac{dx}{dt} &= k_2 y - k_1 x; \qquad & x = n, \text{ if } t = 0; \\ \frac{dy}{dt} &= k_1 x - (k_2 + \lambda) y; \quad & y = 0, \text{ if } t = 0. \end{aligned}\right\}$$

The value of y at any time is

$$y = \frac{nk_1}{2\beta}\left[e^{(\alpha+\beta)t} - e^{(\alpha-\beta)t}\right] \qquad (3),$$

$$\left.\begin{aligned} \text{where } \alpha &= -\frac{1}{2}\,[k_1 + k_2 + \lambda], \\ \beta &= \frac{1}{2}\,\sqrt{(k_1 + k_2 + \lambda)^2 - 4k_1\lambda} \end{aligned}\right\} \qquad (4).$$

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[1] *Loc. cit.*

When $4k_1\lambda$ is very small as compared with $(k_1 + k_2 + \lambda)^2$, equation (3) takes the form of equation (1); otherwise it has the form of equation (2). If we make $\lambda = 0$, or $k_2 = 0$, and $4k_1\lambda$ small, equation (3) becomes

$$y = \frac{nk_1}{k_1 + k_2}\left[1 - e^{-(k_1 + k_2)t}\right], \text{ or } y = \frac{nk_1}{k_1 + \lambda}\left[1 - e^{-(k_1 + \lambda)t}\right],$$

and values of k_1, and k_2 or λ, as the case may be, can be found consistent with the observations in all cases observed, except for 36° with radium. When for this latter case, we give $4k_1\lambda$ the value necessary to make $\alpha + \beta = -0.06$, and $\alpha - \beta = -0.31$, as is required by the last column of Table IV., it is soon seen from the form of equations (3) and (4) that the minimum value of k_1 possible is far too large to give numbers for y in keeping with observed values. Accordingly this explanation of what is going on had to be abandoned.

Another explanation was found more amenable, that the third product is formed, not from the free iodine, but from the hydriodic acid. Call λ, now, the rate of formation of this product. With the same notation, otherwise, as before, our equations take the form

$$\left.\begin{aligned} \frac{dx}{dt} &= k_2 y - (k_1 + \lambda)x\,; & x &= n, \text{ if } t = 0; \\ \frac{dy}{dt} &= k_1 x - k_2 y\,; & y &= 0, \text{ if } t = 0. \end{aligned}\right\}$$

The value of y at any time now is

$$y = \frac{nk_1}{2\beta}\left[e^{(\alpha + \beta)t} - e^{(\alpha - \beta)t}\right] \qquad (5),$$

$$\left.\begin{aligned} \text{where } \alpha &= -\frac{1}{2}(k_1 + k_2 + \lambda), \\ \beta &= \frac{1}{2}\sqrt{(k_1 + k_2 + \lambda)^2 - 4k_2\lambda} \end{aligned}\right\} \qquad (6).$$

These equations are of the same form as equations (3) and (4), except that $4k_2\lambda$ enters, instead of $4k_1\lambda$, as the quantity upon which the form of the curve in y and t turns. As before, we get equations of the type of equation (1) when $4k_2\lambda$ is exceedingly small as compared with $(k_1 + k_2 + \lambda)^2$, and of the type of equation (2) when this is not so. Moreover, the values of y, being directly proportional to k_1, can now be made to agree with those observed for radium at 36° as well as for the other five cases, because now the determining quantity $4k_2\lambda$ does not contain k_1. It will be noticed that the quantities k_2 and λ are interchangeable in equations (5) and (6), so that it will be impossible to distinguish between them, when the equation is applied to our observations, without some other evidence. The following table contains the values of the constants which, when put in equation (5), will be in agreement with the experimental observations.

Table V.

	12°		24°		36°	
	No radium.	Radium.	No radium.	Radium.	No radium.	Radium.
k_1	0.00040	0.00061	0.00081	0.00110	0.00192	0.00249
k_2 (or λ)	0.07	0.07	0.175	0.175	0.70	0.31
λ (or k_2)	small	small	small	small	small	0.06
$k_1+k_2+\lambda$	0.0704	0.0706	0.1758	0.1761	0.7019	0.3725
a	1.92	2.90	1.54	2.10	0.92	3.30

Some idea of the size of the smaller of the two quantities k_2 and λ, in the neighborhood of 12°, may be had from the fact that we saw that at 15° there was no decrease of the amount of iodine after the lapse of 1100 hours when the radium was not present. Taking the case of no radium at 12°, and assuming that $k_2\lambda$ has a value, even if small, equation (5) becomes

$$y = \frac{nk_1}{2\beta}\left[e^{-\frac{k_2\lambda}{k_1+k_2+\lambda}t} - e^{-(k_1+k_2+\lambda)t}\right],$$

approximately. If $\frac{k_2\lambda}{k_1+k_2+\lambda}$ 1100 is as great as 0.01, since one of the factors, k_2 or λ, is about equal to $k_1 + k_2 + \lambda$, the other is of the order of magnitude of 0.00001, at most, and probably much smaller. Further work is now in progress which, it is hoped, will make it possible to determine whether k_2 or λ is the small quantity.

The chief justification for considering the reactions involved as monomolecular is that this supposition gives an explanation consistent with the observed behavior. The recombination of the hydrogen and iodine is at first sight bimolecular, but if the solution contains a large number of free hydrogen ions the action would appear monomolecular. Similarly, if the sulphuric acid takes part in the formation of the third product, that reaction might well appear monomolecular, as the concentration of the acid would not vary materially. It may also be worthy of notice that if the equilibrium value of HI formed by the action of the acid on the iodide were less than the possible maximum, 336, but were reached in a relatively short time, our equation would hold for a large number of hours to a fair degree of approximation. This would make it necessary to put for n in equation (5) a number smaller than 336, and would make all our values of k_1 proportionately greater.

The following general conclusions can be drawn from the numbers in Table V.:

1. The rate of transference, k_1, of HI into H and I, both in the presence and in the absence of radium, increases with increase of temperature.

2. At any temperature, the rate of transference, k_1, of HI into H and I is increased by the presence of radium; the effect of the radium is relatively smaller, the higher the temperature.

3. The constant of the larger of the two retarding factors which keeps down the amount of iodine present at any time (whether it is k_2 or λ, we do not know) increases with increase of temperature, and to a greater extent than does the accelerating constant k_1.

4. The constant of the larger of the two retarding factors is very slightly affected by the presence of radium at the lower temperatures.

5. Whereas at the lower temperatures the action of the radium increases the rates of the accelerating and retarding actions, at 36° it introduces an entirely new (or magnifies a previously existing infinitesimal) retarding reaction, at the same time reducing the retarding action already existing.

Effect of Temperature.

In order to show the effect of temperature alone, both when the solution is under the influence of radium and without it, the reaction was allowed to proceed for ten hours at various temperatures. The results were as follows:

Table VI.

Temperature C.	No. of cc. of N/1250 $Na_2S_2O_3$ solution required in titration when the decomposition of hydriodic acid solution takes place in the dark in the presence of no radium.	radium.	Difference.
0	0.20	0.78	0.58
4	0.45	1.02	0.57
8	0.68	1.21	0.53
12	0.95	1.43	0.48
16	1.20	1.73	0.53
20	1.25	1.75	0.50
24	1.23	1.73	0.50
36	0.93	1.65	0.72
Mean of all differences except that for 36°,			0.53

These observations are plotted in Fig. II. It will be noticed that these temperature curves run parallel from 0° to about 25°, but that thereafter the no radium curve begins to drop faster than the radium curve. This change from parallelism is evidently coincident with the appearance of the change of

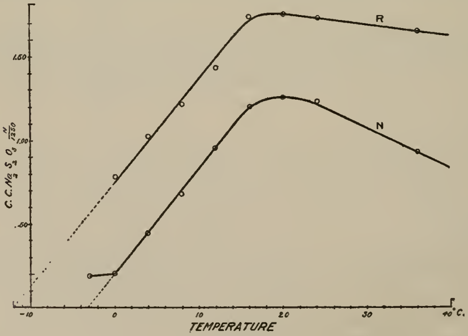

Fig. II.

type of the radium curve which we saw was so noticeable at 36°. It seems from the measurements at hand that the temperature curves would exhibit this same parallelism up to 25° for any number of hours less than 10 during which the reaction is observed; but as the time of observation is taken longer the amount by which the radium curve is higher than the no radium curve falls off with the temperature, and they are not parallel at any part of their course. It is worthy of notice that if we had based our conclusions as to the behavior of radium on a study of the temperature curves for any period of time up to 10 hours at ordinary temperatures, we should have been tempted to say that the action of radium was a purely additive one and that the radium had its own separate action apart from that which was going on in its absence, whereas consideration of the values of the constants in Table V. leads us to believe that the action of radium is intensive, and not additive, at least for ordinary temperatures.

It is further worthy of notice that for the range 0° to 16° the curves are straight lines. If these lines were produced they would cut the axis of temperatures at —12° for radium, and —3.°2 for no radium; that is, if these lines remain straight, the decomposition at the end of 10 hours would be zero if the solution is kept at —12° in the presence of radium, but it would be zero at —3°.2 with no radium. It was out of the question to keep the solution at —12° without freezing, but it was not difficult to keep it at about —3° for a time. This was done by placing the solution in a bath of very dilute alcohol surrounded by a freezing mixture. At the end of 10 hours it was found that the solution without radium had decomposed to the extent of 0.19 cc. of thiosulphate solution. Hence the curves at about 0° must cease to be straight lines and begin to run asymptotically toward the axis of temperature.

Action of γ-Rays Alone.

Hardy and Wilcocks[1] have shown that the γ-rays from radium accelerate slightly the decomposition of iodoform, but that the acceleration is small as compared with that due to the β-rays. In order to determine whether γ-rays behave in a similar way upon the hydriodic acid reaction under consideration, the rays from radium were made to pass through 6 mm. of lead before entering the solution. This thickness of lead is sufficient to absorb all but the very fastest β-rays, and does not absorb appreciably the γ-rays. The reaction was first allowed to go on for ten hours at 24° C., when the amount of free iodine was found to be equivalent to 2.10 cc. of thiosulphate solution. For the sake of comparison the results for ten hours at this temperature are here grouped:

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[1] *Loc. cit.*

No radium for 10 hours at 24°, 1.23 cc. N/1250 $Na_2S_2O_3$ solution.

β + γ-Rays for 10 hours at 24°, 1.73 cc. N/1250 $Na_2S_2O_3$ solution.

γ-Rays for 10 hours at 24°, 2.10 cc. N/1250 $Na_2S_2O_3$ solution.

We thus see that in this case there is much more free iodine when the γ-rays alone act than when the β-rays act along with the γ-rays. The chief difference between the conditions of the last experiment and the other two is that the radium was about 5 mm. further away from the solution when the γ-rays alone were used. The effect of this would have been to reduce the amount of decomposition, and not to increase it, as actually happened. The only other difference in conditions is the introduction of secondary radiations from the lead used to cut off the β-rays, and we would not expect their effect to more than make up for the β-rays cut out.

This increase in the amount of free iodine observed with the γ-rays alone does not seem, therefore, in accord with the results of Hardy and Wilcocks, nor does it seem at first sight to be reasonable or possible. Further consideration will show, however, that such a result can be quite in keeping with the views before expressed of what is going on. The amount of free iodine at any time is determined by the accelerating influence represented by k_1, and by the two retarding influences represented by k_2 and λ. If one, or both, of these retarding influences is not brought so much into play by the γ-rays alone as by the β- and γ-rays together, the amount of free iodine would be increased, even if the value of k_1 were as great for the γ-rays alone as for the β- and γ-rays together.

The only other observation made with γ-rays alone was for three hours at 24°. Comparing it with the corresponding ones, we have:

No radium for 3 hours at 24°, 0.65 cc. N/1250 $Na_2S_2O_3$ solution.

$\beta + \gamma$-Rays for 3 hours at 24°, 0.85 cc. N/1250 $Na_2S_2O_3$ solution.

γ-Rays for 3 hours at 24°, 0.72 cc. N/1250 $Na_2S_2O_3$ solution.

In this case the γ-ray effect is intermediate between the other two, but the numbers are too nearly alike to base a conclusion upon them. Further experiments are to be made to decide whether the proposed explanation is the true one.

Influence of Sunlight and Radium in the Absence of Oxygen.

If a hydriodic acid solution, such as was used in the preceding experiments, was entirely freed from air and placed in a tube from which all the air had been removed, it was found that this tube could be placed in the sunlight for any length of time without the solution showing any decomposition. In order to remove all occluded air the tube, before being sealed off, was kept in the dark under a good vacuum for 24 hours, for otherwise it is found that extremely minute quantities of dissolved air will decompose slightly the hydriodic acid.

The same experiment was then tried with radium, instead of sunlight. In order to keep the solution in a vacuum for two or three days, without sealing the radium up in a tube with the solution, the vessel containing the solution with the radium above it, as before described, was placed on a plate under a bell jar connected by a glass tube with a "Geryk" pump. The joint between the jar and plate was sealed with the preparation made by heating together equal parts of India rubber, paraffin, and vaseline. When the vacuum was secured, the bell jar was sealed off from the pump. A delicate manometer connected with the jar showed no change in vacuum at the end of several days. It was found that the radium also produced no effect.

The experiment was tried at room temperature only.

Summary.

1. When prepared with very pure water a hydriodic acid solution decomposes in the dark, reaching an equilibrium value (experiments made up to 36° C.).

2. Ordinary distilled water contains impurities producing some catalytic action which accelerates the decomposition of hydriodic acid solution in the dark, at the same time introducing another reaction which causes the amount of free iodine to reach a maximum value and then fall off indefinitely (experiment made at 15° C. only).

3. At any temperature up to 24° C. more iodine is liberated in any given time from a solution of hydriodic acid in the dark under the influence of radium than from one which is not so influenced.

4. When the experiment is tried at 36° C., this last statement is only true up to 22 hours, for, whereas the amount of free iodine with no radium reaches an equilibrium value, with radium it reaches a maximum and then falls off indefinitely.

5. At 36° C. radium seems to cause the formation of the same third product which impurity in the water produces at low temperature.

6. In general, rise in temperature tends to increase the amount of free iodine at any time, whether radium is used or not.

7. The amount of free iodine at any time depends on three quantities: an accelerating factor depending upon the rate at which HI breaks up into H and I; and two retarding factors, the one depending upon the rate at which H and I recombine and the other upon the rate at which HI enters into another reaction. One of these two retarding factors is not appreciable for temperatures as low as 24° C. (see conclusions after Table V.).

8. The γ-rays alone cause more iodine to be set free than

do the β- and γ-rays together; this is probably due to the β-rays increasing the retarding factors more than do the γ-rays (experiment made at 24° C. only).

9. Neither sunlight nor radium causes decomposition of hydriodic acid solution in the absence of oxygen (experiments made at room temperatures only).

This investigation was carried out in the chemical laboratory of Dalhousie University, and in conclusion we wish to thank Professor E. Mackay for his suggestions and valuable criticisms during the progress of the work.

Dalhousie University,
Halifax, N. S.,
October 15, 1907.

[Contributions from the Chemical Laboratory of Harvard College.]

SOME DERIVATIVES OF TETRACHLORORTHOBENZOQUINONE.

By C. Loring Jackson and P. W. Carleton.

This paper contains an account of the continuation of the work on tetrachlororthobenzoquinone begun by Dr. MacLaurin and one of us.[1]

If equal weights of tetrachlororthoquinone and tetrachlorpyrocatechin, dissolved in the smallest possible amounts of hot chloroform, are mixed and the mixture cooled as quickly as possible, black needles of octochlororthoquinhydrone are deposited; but if, instead, the mixed solutions are kept warm for some time, the product is the yellow heptachlororthoquinopyrocatechin hemiether, the formation of which is accompanied by evolution of hydrochloric acid.

The orthoquinhydrone, dried *in vacuo*, gave, on analysis, percentages of chlorine corresponding to the formula

$$C_6Cl_4O_2C_6Cl_4O_2H_2.\frac{1}{2}H_2O.$$

As it is decomposed by heat we could not determine the amount of water directly, but think we are right in assigning this formula to it for the following reasons. Since five analyses of different specimens gave concordant results, the low percentage of chlorine must be due to a constant constituent rather than to a mixture with an impurity. Further, the only probable impurity which could lower the percentage of chlorine is the heptachlor hemiether, and our quinhydrone must have contained about 25 per cent of this substance to reduce the percentage of chlorine to that found, but it would be impossible that such a quantity of a yellow impurity could be overlooked among the well formed, shining, black needles of the quinhydrone. The quinhydrone is also formed when benzene is used as the solvent instead of chloroform, and we have observed no tendency to the formation of the hemiether in benzene solution. We can therefore reject an admixture of the hemiether as an explanation of the low percentages of chlorine. The only other theory we can find is that they must be caused by the addition of some substance to the molecule and as this substance is added both in chloroform and benzene solution, it can be nothing but water. This conclusion is confirmed by the fact that the crystals effloresce on drying; and, further, Russe and one of us[1] found that the octobromorthoquinhydrone crystallizes with one molecule of water, so that there is good reason to expect that the chlor compound would behave in the same way. In fact, we think it probable that our compound also crystallizes with one molecule of water, half of which is given off on drying *in vacuo*, thus explaining the effloresced appearance of the dried compound, but unfortunately, this idea occurred to us so late that we could not test it by experiment. It is certainly surprising that these compounds should take up water from ordinary chloroform or benzene, but this striking attraction for water, enabling the substance to abstract it even from liquids containing only traces of it, has been observed more than once with derivatives of the orthoquinones.[2] The quinhydrone turns yellow when heated to 70°, probably from the formation of the hemiether, and seems to be dissociated into its components, when dissolved, as would be expected from what is known of paraquinhydrones.[3]

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[1] This Journal, 37, 7 (1907); 38, 120 (1907).

[1] This Journal, **35**, 174 (1906).
[2] *Ibid.*, **31**, 109 (1904).
[3] Torrey and Hardenbergh: This Journal, **33**, 167 (1905).

The heptachlororthoquinopyrocatechin hemiether,

$C_6Cl_4OHOC_6Cl_3O_2$,

crystallizes, with some difficulty, in scales, melting with decomposition at 214°. Its most striking property is its strong tendency to lose a molecule of hydrochloric acid and pass into the red ether $C_6Cl_4O_2C_6Cl_2O_2$. This change takes place slowly and partially, even at ordinary temperatures if it is exposed to air and light, more rapidly on heating, and is also brought about by the action of alcohol. Neither of these reactions, however, ran quantitatively, as a specimen heated to 110°–140°, although it lost quickly about half of the calculated amount of hydrochloric acid, retained the second half so firmly that even after 8 weeks' heating we did not succeed in bringing the loss much above 75 per cent of the theory. With alcohol the loss was a little less than 67 per cent, and in this case impurities were detected in the red ether, pointing to the occurrence of secondary reactions. This result is certainly unexpected, as the formula of the hemiether seems to require a quantitative transformation.

MacLaurin and one of us,[1] by the action of benzaldehyde or acetone on tetrachlororthoquinone, obtained a yellow product, which was supposed to be this heptachlor hemiether, but seemed so unstable that it could not be purified or studied. It has happened before in work with the orthoquinones that an impure product was converted into the red ether $C_6Cl_4O_2C_6Cl_2O_2$ by conditions which did not affect the pure substance.

We have found easy methods for the preparation of two of the substances discovered by MacLaurin and one of us. Thus the hexachlororthoquinomethylmonohemiacetalpyrocatechin ether,[2] $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, melting at 198°, can be made by boiling the ether $C_6Cl_4O_2C_6Cl_2O_2$ with methyl alcohol; and the hexachlororthoquinomethylhemiacetalpyrocatechin ether,[3] $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, melting at 218°, can be made by the action of sodic methylate on the same ether.

[1] This Journal, **37**, 10 (1907).

[2] *Ibid.*, **38**, 150 (1907).

[3] *Ibid.*, **38**, 154 (1907).

The monohemiacetal melting at 198° was converted into a methylacetacetal, $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$, melting at 220°, by treatment with acetic anhydride. This substance was prepared by MacLaurin and one of us,[1] who found the melting point 215°, but supposed that it had the composition of a diacetoxypyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)_2$, since the only chlorine determination made agreed with this (calculated Cl = 42.01. Found, Cl = 42.49. $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$, Cl = 43.03), and its formation seemed to have been preceded by the conversion of the hemiacetal into the red orthoquinopyrocatechin ether. The work described in this paper showed that the red impurity appearing during the action of acetic anhydride is not the ether, and is formed in such small amount as not to influence the nature of the product; and our analyses prove that the main product is the acet compound, $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$, thus furnishing a welcome confirmation of the monomethylhemiacetal formula, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, ascribed to the mother substance on grounds which were not absolutely convincing.

A set of preliminary experiments has made it probable that acetophenone enters into a compound with tetrachlororthoquinone; and another set, in which tetrachlorpyrocatechin was oxidized with fuming nitric acid containing a little hydrochloric acid, gave a yellow product, which may be identical with the substance isolated by MacLaurin and one of us[2] from the mother liquors of the tetrachlorpyrocatechin preparation, after they had stood seven months with an excess of chlorine. It is hoped that both these substances will be studied in this laboratory in the coming year.

EXPERIMENTAL.

Preparation of Tetrachlororthobenzoquinone.—The method adopted for making the tetrachlorpyrocatechin was that described by MacLaurin and one of us.[3] In the hope of avoiding a large use of glacial acetic acid, some experiments were

[1] THIS JOURNAL, **38**, 153 (1907).

[2] *Ibid.*, **37**, 19 (1907).

[3] *Ibid.* **37**, 11 (1907).

tried on purifying it with alcohol but, although good results were obtained, we found it more satisfactory to return to the crystallization from glacial acetic acid. Successive portions were recrystallized from the same quantity so as to reduce the amount washed in the mother liquors and the use of the expensive solvent. The yield in this case was quantitative after the first crystallization, and the product remained of satisfactory color and melting point during a large number of operations. After the acetic acid became so loaded with impurities as to give colored crystals, it was distilled, and in this way the greater part of it recovered. The glacial acetic acid in which the tetrachlorpyrocatechin was made was also recovered by distillation. In either case the residue was a black, tarry mass too impure to make it worth while to try to extract any tetrachlorpyrocatechin from it.

In converting the tetrachlorpyrocatechin into the corresponding quinone, a considerable saving of glacial acetic acid was effected by adopting the method found by Flint[1] to work well with the tetrabromorthoquinone. The tetrachlorpyrocatechin was dissolved in alcohol, using 1 or 1.5 parts of solvent to 1 part of the solid, and to this solution was added fuming nitric acid diluted with 6 parts of glacial acetic acid, the process being identical with that of MacLaurin in other respects. This method worked well if the amount of substance was small and the temperature was kept low. The yield was from 75–80 per cent of the theory (MacLaurin obtained 81.5 per cent), and, although the melting point of the product was not above 127° (MacLaurin's average was 133°), it was pure enough for our purposes.

Octochlororthobenzoquinhydrone, $C_6Cl_4O_2C_6Cl_4O_2H_2.\frac{1}{2}H_2O$.—This substance was made by dissolving equal weights of tetrachlorpyrocatechin and tetrachlororthoquinone separately in small quantities of hot chloroform, mixing the two solutions and cooling rapidly, when a large quantity of long, black needles separated. The crystals were filtered out, dried on filter paper and then *in vacuo* over sulphuric acid and soft paraffine, when they lost their brilliant lustre, turning to a dull purple.

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[1] THIS JOURNAL, **39**, 83 (1908).

In preparing this compound the operations must be carried through as rapidly as possible since, if the substance was allowed to stand with the chloroform, especially if it was hot, the yellow heptachlororthoquinopyrocatechin hemiether (described later) was formed. If benzene was used as the solvent, the quinhydrone was also obtained (Analysis IV.), but in this case there was a tendency for part of the constituents to remain uncombined. As the substance could not be dissolved without decomposition, it was analyzed with no attempt at purification.

I. 0.2106 gram substance gave 0.4828 gram AgCl.
II. 0.1688 gram substance gave 0.3878 gram AgCl.
III. 0.1548 gram substance gave 0.3530 gram AgCl.
IV. 0.1818 gram substance gave 0.4136 gram AgCl.
V. 0.1694 gram substance gave 0.3889 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_4O_2H_2.\frac{1}{2}H_2O$.	Found. I.	II.	III.	IV.	V.
Cl	56.46	56.68	56.79	56.39	56.26	56.74

These analyses agree with each other and the theory as closely as was to be expected with a substance that could not be purified. The reasons for adopting the formula with $\frac{1}{2}H_2O$ have been given in the introduction. We will only add here that to get a corresponding percentage of chlorine, 56.67, from the presence of the heptachlor hemiether, there must have been 25 per cent of this impurity.

Properties of Octochlororthobenzoquinhydrone.—It crystallizes in shining, black needles, which effervesce easily, becoming dull and of a dark-purple color. At 70° it turns yellow, probably from the formation of heptachlororthoquinopyrocatechin hemiether, and then melts to a red liquid at about 160°. It dissolves in ethyl or methyl alcohol, chloroform, benzene, toluene or nitrobenzene, but seems to be decomposed by solution, as is to be expected from its analogy with the paraquinhydrone. This decomposition seems less complete when the solvent is chloroform, benzene or toluene than with the alcohols or nitrobenzene, but this is probably due to the fact that the quinhydrone is formed again more easily from its constituents in the first set of solvents than in the last. The treatment with nitrobenzene yields three products, probably the following: a white one, tetrachlorpyrocatechin; a red one, a mixture of tetrachlororthoquinone and the red ether $C_6Cl_4O_2C_6Cl_2O_2$; and a yellow heptachlororthoquinopyrocatechin hemiether.

Heptachlororthoquinopyrocatechin Hemiether, $C_6Cl_4OHOC_6Cl_3O_2$. —This substance was made by mixing hot solutions of equal parts of tetrachlororthoquinone and tetrachlorpyrocatechin in small amounts of chloroform and allowing the mixture to remain hot for about half an hour. Hydrochloric acid was given off and the yellow product deposited as the solution cooled, with an additional amount on evaporation. Chloroform with tetrachlororthoquinone alone gave no reaction. The yellow product was purified by crystallization from hot chloroform, or ligroin, for, although only slightly soluble in the latter when hot, it is insoluble in it when cold. It was dried *in vacuo* for analysis.

I. 0.1489 gram substance gave 0.1735 gram CO_2 and 0.0866 gram H_2O.

II. 0.1398 gram substance gave 0.3094 gram AgCl.

III. 0.1642 gram substance gave 0.3614 gram AgCl.

IV. 0.1716 gram substance gave 0.3770 gram AgCl.

V. 0.1836 gram substance gave 0.4056 gram AgCl.

VI. 0.2048 gram substance gave 0.4491 gram AgCl.

	Calculated for $C_6Cl_4OHOC_6Cl_3O_2$.	Found. I.	II.	III.	IV.	V.	VI.
C	31.47	31.78	...	...	...	...	...
H	0.22	1.24	...	...	...	...	...
Cl	54.31	...	54.72	54.42	54.32	54.63	54.22

The specimen used in VI. was crystallized from ligroin, the others from chloroform.

The molecular weight was determined by the boiling point method.

I. 0.1030 gram substance dissolved in 37.5 grams C_6H_6 gave $\Delta = 0.^\circ 017$.

II. 0.3167 gram substance dissolved in 32.8 grams C_6H_6 gave $\Delta = 0.^\circ 055$.

	Calculated for $C_6Cl_4OHOC_6Cl_3O_2$.	Found. I.	II.
Mol. wt.	457.5	421.7	458.1

Properties of the Heptachlororthoquinopyrocatechin Hemiether.—It crystallizes with some difficulty from chloroform in yellow scales, but in the earlier crystallizations of the impure substance good-sized square blocks were also observed. It decomposes on melting, as shown by its turning red, and the highest temperature at which we have observed these phenomena is 214°, but a specimen melting, or, rather, decomposing, at a much lower point, gave good results on analysis. The decomposition with reddening takes place very easily, in fact, slowly and partially, by mere exposure to the air and light, and more rapidly by heating, so that it is easy to see that the melting point would be very much influenced by the way in which the heat was applied. To study this reaction more carefully, 1.0782 grams of the substance were heated to 110°–140°. At first the loss was rapid, but after about half the theoretical amount of hydrochloric acid had been given off, the action became very slow, and was finally stopped after 8 weeks, although the weight was not absolutely constant. The residue weighed 1.0126 grams instead of the 0.992 gram expected from the reaction:

$$C_6Cl_4OHOC_6Cl_3O_2 = C_6Cl_4O_2C_6Cl_2O_2 + HCl.$$

The loss, therefore, is 76.28 per cent of the theoretical. It is hard to understand, with the formula ascribed to this substance, why the loss should not be quantitative and rapid. Ethyl or methyl alcohol or ether (unpurified ether containing some alcohol) decomposes it with reddening. After one failure to get a quantitative yield of the red ether by heating the compound, we tried the action of ethyl alcohol on it in hope of a better result, but the loss in this case was only 66.67 per cent of the theoretical and the red ether was contaminated with a soluble impurity, pointing to a secondary reaction. With methyl alcohol the amount of impurity seemed to be even larger. It is soluble in chloroform or benzene; essentially insoluble in cold, slightly soluble in hot ligroin; slightly soluble in nitrobenzene. Chloroform stood with it in the cold for over a month with no signs of any reaction, and this solution could even be boiled for a short time without much decomposition. Cold water did not dissolve it, but on long standing with it took on the purple color of a solution of chloranilic acid. Strong sulphuric acid showed no reaction with the heptachlor compound in the cold but, on warming, gave a dark-green, almost black color. Sodic hydrate also turned the hemiether black, forming a yellowish-green solution, though the amount dissolved was very small.

Hexachlororthoquinomethylmonohemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—This substance has been described by MacLaurin and one of us,[1] but we have succeeded in improving the method of preparation, so that it can now be made quickly and easily. For this purpose the red ether,[2] $C_6Cl_4O_2C_6Cl_2O_2$, was boiled with methyl alcohol in a flask with a return condenser for a few minutes, the hot liquid was then poured off and replaced with fresh methyl alcohol and this process repeated until the ether was converted entirely into its hemiacetal, which took place in less than an hour. The product was nearly pure and the yield not far from quantitative. This method is, therefore, better than letting the ether stand in the cold with methyl alcohol, as recommended before. It was purified by crystallization from a mixture of equal parts of benzene and ligroin until it showed the constant melting point 198°. During the crystallization it was noticed that at first rhombic plates were formed, which, on the third crystallization, were converted into the characteristic clusters of needles. This phenomenon was observed only with specimens prepared from the red ether. To be sure that one product was the hemiacetal a sample was analyzed and gave 47.34 per cent Cl instead of 47.01.

Hexachlororthoquinomonomethylacetacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$.—This substance was prepared by MacLaurin and one of us,[3] but on the strength of a single analysis a different composition was ascribed to it. One of the principal observations which led to a wrong conclusion in regard to this substance was the formation of a red product, supposed to be the ether, $C_6Cl_4O_2C_6Cl_2O_2$, and to constitute an intermediate stage in the reaction. Our later work has shown that this red substance is tarry and easily soluble in benzene, so that it cannot be the ether, and also that it was not formed in nearly so large amount as was supposed at first.

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[1] This Journal, **38**, 150 (1907).

[2] *Ibid.*, **37**, 12 (1907).

[3] *Ibid.*, **38**, 153 (1907).

The acet compound was best prepared by warming the hemiacetal melting at 198° with acetic anhydride on the steam bath for two hours, and allowing the hot liquid to cool. The crystals thus obtained were especially pure. An additional amount of somewhat poorer quality was obtained by evaporating off the anhydride from the remaining solution. The purification was effected by crystallization from equal parts of benzene and ligroin until it showed the constant melting point 220°.

The same product was obtained by heating the hemiacetal with acetic anhydride until all the anhydride had evaporated, or by heating it for 20 minutes and then removing the excess of anhydride with a blast of cold air. It was dried *in vacuo* for analysis.

I. 0.2925 gram substance gave 0.3930 gram CO_2 and 0.0430 gram H_2O.

II. 0.1748 gram substance gave 0.3034 gram AgCl.

III. 0.1697 gram substance gave 0.2949 gram AgCl.

This is the analysis given in the paper by MacLaurin and one of us.

	Calculated for	Found.		
	$C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$.	I.	II.	III.
C	36.38	36.64	...	...
H	1.21	1.63	...	...
Cl	43.03	...	42.92	42.49

The substance forms masses like a cauliflower of a lighter yellow color than the hemiacetal and melts at 220° to a light-brown liquid. MacLaurin found 215°.

Attempts to convert this acet compound into the phenylhydrazone did not lead to the desired result for, although a reaction seemed to take place, it was evidently not the simple replacement of oxygen which we had expected.

Hexachlororthoquinomethylhemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.—This substance, which melts at

218°, was discovered by MacLaurin and one of us,[1] but no convenient way was found for preparing it. We have worked out the following method, similar to that used by Shaffer and one of us[2] with the bromine compound, by which it can be made in a few minutes instead of several months; but, unfortunately, this was done at the very end of the year, when no time was left for the study of the material thus obtained. The tetrachlororthoquinopyrocatechin ether was mixed with a methyl alcohol solution of sodic methylate (made by treating 50 parts of the alcohol with one of sodium), which was added slowly until the ether just went into solution. The mixture was then barely acidified with sulphuric acid, more methyl alcohol added, and the whole heated. The sodic sulphate was filtered out of the hot solution, and, as the filtrate cooled, it deposited white crystals of the desired product, mixed with a small amount of a yellow impurity, apparently the monohemiacetal, melting at 198°. Four crystallizations from hot methyl alcohol were sufficient to purify it, as shown by the constant melting point 218°.

Two sets of preliminary experiments may be described here. Tetrachlororthoquinone, mixed with half its weight of acetophenone, turned yellow after standing 2 or 3 days. The product, washed with ligroin and crystallized from a mixture of benzene and ligroin, melted at 281°, contained 42.90 per cent of chlorine, and was essentially insoluble in alcohol, even when hot. The tetrachlororthoquinone, therefore, did not behave like the tetrabromorthoquinone under these conditions, as that gives[3] the ether $C_6Br_4O_2C_6Br_2O_2$, its reduction product, $C_6Br_4O_2C_6Br_2(OH)_2$, and the hemiether $C_6Br_4OHOC_6Br_3O_2$, whereas our product melts too high for the hemiether and too low for the complete ethers, and contains 8 per cent less chlorine than they do. This is the more unexpected as MacLaurin and one of us[4] obtained, from the action of acetone on the tetrachlororthoquinone, three products which seemed to correspond to the bromine compounds mentioned above. These experiments will be continued in this laboratory.

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[1] This Journal, **38**, 154 (1907).

[2] *Ibid.*, **34**, 463 (1905).

[3] *Ibid.*, **35**, 170 (1906).

[4] *Ibid.*, **37**, 10 (1907).

If tetrachlororthoquinone (or pyrocatechin) was heated with fuming nitric acid to which a little strong hydrochloric acid had been added and the heating was stopped when a reddish tar had collected at the bottom, a substance was obtained which was purified as follows: The mixture was allowed to stand overnight and then, after diluting it with water, was heated on the steam bath with frequent stirring, which converted the red tar to a yellow solid. This was washed with alcohol and crystallized from a mixture of about 3 parts of alcohol to 2 of benzene, or from glacial acetic acid, until it melted at 146°–147°. The product obtained in this way consisted of long, yellow prisms mixed with yellow rhombic plates, and therefore we feel no certainty that it was pure. Two preliminary analyses were made, however; one, mostly prisms, gave Cl 62.72 per cent, the other, which contained more plates, Cl 61.83 per cent. More work is obviously necessary before its nature can be determined, but it shows a strong resemblance to a substance obtained by MacLaurin and one of us[1] by the long continued action of chlorine in acetic acid solution on tetrachlorpyrocatechin. This melts at 146°–147°, crystallizes sometimes in yellow needles, sometimes in yellow plates, and contains 63.06 per cent of chlorine. An abnormal quinone, $C_6Cl_5HO_2$, contains Cl 62.84, but it would be unsafe to assign this formula to either of these products upon our present data. The formula $C_5Cl_4O_2$, which the substance would have if it corresponds to the bromine compound,[2] contains Cl 60.88. In preparing our yellow product success depends on stopping the boiling with nitric acid at just the right point. If stopped too soon, the product remains obstinately tarry; if carried on too long, it is converted almost completely into oxalic acid. We can give only two indications of the point at which the action should be stopped: a red tar should appear at the bottom of the liquid and the chlorine should have ceased to come off rapidly from the mixture, but even with these indications the point was so hard to determine that we could not invariably succeed in preparing the yellow product. On one occasion a white substance was also obtained, which burnt with a smoky flame and gave a test for halogen when heated on a copper wire. This may be analogous to the white acid obtained from the tetrabrompyrocatechin in a similar way by Russe and one of us.[1] The work will be continued in this laboratory.

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[1] This Journal, **37**, 19 (1907).

[2] *Ibid.*, **35**, 184 (1906).

CAMBRIDGE, MASS.,
August 16, 1907.

ON SOME CUPRAMMONIUM SALTS. VI.[2]

BY DAVID W. HORN AND MINNIE A. GRAHAM.

The object of this paper is to describe a case of isomerism met with in the course of a study of cuprammonium salts. Up to the present, isomerism has not been known in this group of compounds.

The isomeric substances in question are represented by the formula

$$Cu(OOC)_2.2NH_3.$$

One of these was described in a previous paper.[3] It has since been found to be characterized by exceptional chemical inactivity under certain circumstances. It can be kept in an atmosphere of dry ammonia gas for at least one month without change in weight, and it remains unchanged under liquid ammonia throughout several hours. In other words, it acts as a *saturated* compound toward ammonia. For the sake of clearness, this oxalate will be referred to hereafter as the α-compound.

This apparent saturation was unexpected and suggested the existence and preparation of an *unsaturated* compound of the same composition. The pentammine oxalate described in a previous paper undergoes dissociation, under the proper conditions, as follows:

$$Cu(OOC)_2.5NH_3 \rightleftarrows 3NH_3 + Cu(OOC)_2.2NH_3.$$

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[1] THIS JOURNAL, 35, 186.

[2] Read in abstract at the meeting of the American Chemical Society at Toronto, June 28, 1907.

[3] THIS JOURNAL, 35, 275 (1906).

Since dissociations are reversible, the diammine oxalate prepared in this way should differ from the α-compound in that it should react readily with ammonia. We shall refer to such an unsaturated diammine oxalate as the β-compound.

We prepared the β-diammine oxalate from the pentammine salt and the pentammine oxalate for this purpose from the monammine oxalate.

The monammine oxalate, we find, is best prepared as follows: 7.6 grams of air-dried copper oxalate are warmed with 45 cc. of ammonia water of sp. gr. 0.9 until solution is complete. The solution is poured gradually and with constant stirring into 2250 cc. of water. The diluted solution thus obtained is set aside in evaporating dishes. The monammine salt separates out after the lapse of from 1 to 3 days, depending upon the area of the free surface of the evaporating liquid. The salt is dried in the air. The following analyses served for identification:

Weight taken for analysis. Grams.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found. Per cent.	Percentage calculated for $Cu(OOC)_2.NH_3$. Per cent.
1.5038	43.64	9.92	10.11
0.6951	20.49	10.06	...

When the monammine salt is placed in dry ammonia gas at 1 atmosphere pressure and ordinary temperatures, the color begins to change at once and the weight increases. After some time, the increase in weight ceases. The following figures show that the reaction is to be represented by the equation

$$Cu(OOC)_2.NH_3 + 4NH_3 \rightleftarrows Cu(OOC)_2.5NH_3:$$

Weight monammine salt taken. Grams.	Time in ammonia gas. Hours.	Percentage gain in weight.	Percentage calculated for above equation.
0.4987	96	38.98	40.46
0.2624	48	38.87	...
2.3091	72	39.65	...
2.3879	15	39.08	...

The first attempts to dissociate the pentammine oxalate into the β-compound were made at +90°. It was heated, in a boat, in a tube that was sealed at one end and was closed at the other by a rubber stopper with one perforation, through which passed an L-shaped delivery tube so arranged that its outer end dipped just beneath the surface of mercury.

The product obtained by heating under these conditions to constant weight had the composition of a diammine oxalate as is shown by the following analyses:

Weight taken for analysis. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2.2NH_3$. Per cent.
0.2032	10.73	18.03	18.38
0.1670	9.29	18.98	...
0.4566	23.72	18.14	...

This product was sky-blue, whereas the α-compound has a brilliant sapphire color. The sky-blue color soon changed to darker blue and purple shades when the product was placed in dry ammonia gas, indicating addition was taking place under the same conditions under which the α-compound remains unchanged. Differences in the state of subdivision might be considered as the cause of the difference in color, and differences in the properties of the surfaces of the substances, as the cause of the different behavior toward ammonia gas. To determine whether the differences were superficial or deeper seated, the specific gravity of the α-compound and of the product obtained at +90° was determined.

We used specific gravity bottles of 2, 25 and 50 cc. capacity. Since the diammine oxalates are slowly decomposed by water, the specimens were weighed in alcohol, xylene or nitrobenzene. The most concordant results were obtained in the nitrobenzene. The values for the specific gravity of the nitrobenzene are given in the first column of the following table; for that of the α-compound in the second column; and for that of the product obtained at 90° C. in the last column, first three numbers:

Nitrobenzene D^{25}_{4}.	α-Compound D^{25}_{4}.	Dissociation product D^{25}_{4}.
1.2017	2.308	2.224
1.2015	2.308	2.225
1.2016	2.305	2.235
1.2015	2.303	...
1.2014	2.304	2.212
1.2015	2.305	2.227

The difference between the average values for the sp. gr. of the α-compound and for the dissociation product indicates more than a superficial difference between these two substances.

To avoid, as far as possible, any isomerization that may occur at higher temperatures, the dissociation was accomplished at ordinary temperatures. The method consisted in placing the pentammine salt in a desiccator over sulphuric acid until it no longer changed in weight. In the following table are given the successive weights of a specimen of the pentammine salt kept over sulphuric acid. The substance was enclosed in a weighing tube shaped like an Erlenmeyer flask. A rounded glass rod with which the powder was frequently and thoroughly stirred was kept in the weighing tube throughout the experiment.

It has been shown in the preceding paper that the pentammine salt passes to a diammine salt under these conditions. The question whether or not constant weight is finally obtained over sulphuric acid is answered in the following experiment: The pentammine salt used had been prepared for some time and had already lost some of its ammonia. The last four figures show that the final product has an almost negligible dissociation tension of ammonia at the temperature of the experiment, *i. e.*, that of the room:

Time in hours.	Weight in gram.	Loss in weight per hour.
0	0.5952	....
4	0.4864	0.0272
8	0.4843	0.0005
22	0.4764	0.0005
46	0.4743	0.0001
71	0.4733	0.00004
95	0.4732.	0.000004

In preparing larger quantities of the diammine salt, amounting to five grams of more, the pentammine salt was put in a mortar, with its pestle, in a desiccator some 24 cm. in diameter and containing 250 cc. sulphuric acid of sp. gr. 1.84. The mortar was removed frequently and the material in it ground and mixed with the pestle.

The product obtained by this method adds ammonia rapidly when placed in an atmosphere of that gas. Because it has the same composition as the α-compound, yet behaves as an unsaturated body toward ammonia, we shall refer to it as the β-compound. The last two numbers, column 3, preceding table, are the specific gravities of specimens of it.

In order to make a final test of the view that we had here isomeric substances, and that one of these was capable of passing over into the other, we took advantage of the method of determining transition temperatures, already referred to.

In some preliminary experiments made in a melting point tube, the product obtained at +90° had been found to change from sky-blue to light green at about +180°, and to brown at about +220°. The α-compound was found to change from sapphire to dark, olive-green when held in a paraffin bath at about +215°. When examined by the transition point method neither the α- nor the β-compound exhibited any change, whatever below +150° at 3 cm. pressure.

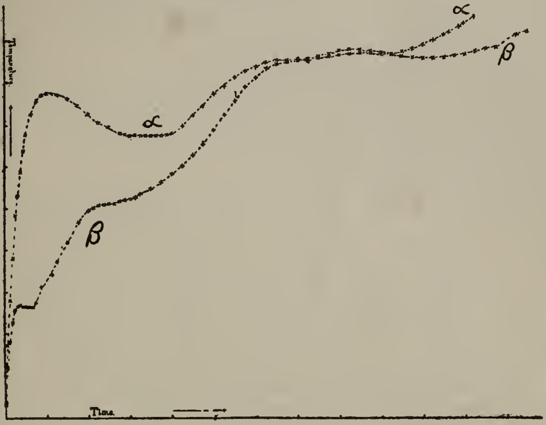
The two substances were then examined by this method at the same pressure at temperatures above +150° C. For this purpose, one end of a long piece of glass tubing was sealed and blown into a small bulb. A thermometer, graduated into tenths and reading from +150° to +206°, was introduced so that its bulb came within the glass bulb at the end of the tubing. Enough α-oxalate was then poured in to cover the bulb of the thermometer, and the tube was clamped in a vertical position. The upper end of the glass tubing was then closed by a rubber stopper with one perforation, through which passed an L-shaped delivery tube, which was connected with a filter pump and a manometer. After the pump was started the glass bulb containing the oxalate surrounding the bulb of the thermometer was immersed in a paraffin bath maintained at +202° to +204°.

After the completion of the experiment with the α-oxalate, it was repeated under exactly the same conditions with the β-oxalate. The results of the two experiments are given in the following table:

Time in minutes.	Thermometer readings		Time in minutes.	Thermometer readings		Time in minutes.	Thermometer readings	
	α.	β.		α.	β.		α.	β.
0	161.4	161.3	22	187.2	180.7	62	194.7	194.5
0.5	166.9	164.8	23	187.1	180.8	64	195.0	194.6
1	171.2	167.2	24	187.0	180.9	66	195.1	194.7
1.5	175.2	169.1	25	187.0	181.1	68	195.0	194.8
2	179.3	170.2	26	187.0	181.4	70	194.8	194.9
2.5	181.2	170.6	27	187.0	...	72	194.6	194.8
3	183.5	170.7	28	187.0	181.9	74	194.6	194.6
3.5	185.5	170.6	29	187.0	...	76	194.8	194.4
4	187.0	170.6	30	187.0	182.5	78	195.1	194.3
4.5	...	170.6	31	187.0	...	80	195.5	194.2
5	189.0	170.6	32	187.2	183.3	82	195.9	194.2
5.5	...	170.6	34	187.9	184.1	84	196.4	194.2
6	190.2	171.0	36	189.0	185.1	85	196.6	...
7	190.8	172.6	38	189.8	186.2	86	...	194.3
8	191.0	...	40	191.0	187.5	87	197.1	...
9	191.0	173.7	42	191.7	189.0	88	197.4	194.4
10	190.9	174.9	44	192.5	190.3	90	198.0	194.7
12	190.5	176.8	46	193.1	191.6	92	...	194.9
14	189.8	178.7	48	193.6	192.6	94	...	195.1
16	189.0	179.8	50	194.0	193.4	98	...	195.4
17	...	180.1	52	194.2	193.9	100	...	195.6
18	188.2	180.3	54	194.1	194.1	...	...	...
19	...	180.4	56	194.3	194.2	...	...	...
20	187.8	180.5	58	194.1	194.3	...	...	...
21	...	180.5	60	194.5	194.4	...	...	...

The data in this table are represented graphically in the following figure.

The curves indicate clearly that the two substances are quite different. The principal differences in their behavior may be seen at a glance. The five transition temperatures are very well marked, considering that the bath was maintained throughout at a temperature so far above them. But this was necessary in order that the two sets of data should be comparable. The irregularity of the curves about +194° is due to the relative violence of the dissociation at this temperature. The solid was thrown in considerable quantities to the upper part of the tube where it often lodged temporarily and always cooled before it fell back into the region about the bulb of the thermometer. In the first experiment, the material that lodged was shaken down at times by tapping the tube with a pencil, and this caused fluctuations that did not occur in the second experiment where the tapping was avoided. Each of the 5 transition temperatures was confirmed in a separate experiment.



Under the given conditions, the sapphire α-compound yields a deep olive-green product at about +187°, while the sky-blue β-compound yields a pale Nile-green product at about 171°. Both the α- and the β-compound yield a dark chocolate-brown body at about the same temperature, +194°, and the product from the one cannot be distinguished by its appearance from that from the other.

We did not have sufficient time to determine the composition of these products, but it is our opinion, in view of the behavior of the diammine sulphate when heated, that the two green products are monammine oxalates, and that the transition point occurring at about 180° in the curve of the β-compound corresponds to the transformation of one monammine oxalate into its isomer. This idea is in accord with the superposition of the two curves at about +194° and with the apparent identity of the brown products finally obtained in both cases. The two green (monammine) oxalates will be examined when the work can be resumed.

It will be recalled that the possibilty of a partial isomerization of the β- into the α-compound under the conditions stated was suggested. This idea was confirmed with a preparation of the diammine salt obtained by heating the pentammine oxalate in the vacuum of a filter pump gradually to 100° and maintaining it at that temperature for some 4 hours. This product, if there had been no isomerization, should have given the heating curve of the β-compound, whereas, if isomerization had occurred, it should have given the curve of the α-compound. The following data were obtained. The transition temperature is +187°.2.

Time in min.	Temp. C.	Time in min.	Temp. C.	Time in min.	Temp. C.	Time in min.	Temp. C.
0	161.5	7	185.7	17.25	188.7	28	187.2
1	164.4	8	186.9	20.5	188.5	29	187.2
2	169.2	9	187.6	21.75	188.2	30	187.2
3	174.1	10	188.1	24	187.2	31	187.2
4	178.4	11	188.5	25	187.2	32	187.2
5	181.7	13	188.7	26	187.2	33	187.2
6	184.2	15.5	188.8	27	187.2	34	187.2

This experiment shows that the β-compound must be the labile isomer and the α-compound the stable one, and that the former may be transformed into the latter when heated to about +100°.

The following table contains a summary of the properties of these two isomers.

a or Stable Form.	β or Labile Form.
Saturated toward ammonia	Unsaturated toward ammonia.
Crystalline[1]	Thus far obtained only in amorphous condition.
D_4^{25} 2.305.	D_4^{25} about 2.230.
Intense sapphire in color.	Sky-blue in color.
Dissociates into a deep olive-green compound at 3 cm. pressure and about +187°.	Dissociates into a pale Nile-green compound at 3 cm. pressure and at about +171° C.
	Passes more or less completely into the *a*-form at about 100° C.

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[1] This Journal, **35**, 275 (1906).

There are indications of isomerism in diammine salts of other dibasic acids; for example, the *saturated* diammine carbonate is already known.[1]

ON THE THEORIES OF CATALYSIS: A REPLY TO JULIUS STIEGLITZ.

[EIGHTH COMMUNICATION ON CATALYSIS.]

By S. F. Acree.

Mr. Stieglitz's reply in the March number of THIS JOURNAL absolutely confirms the accusations which I made against him in January. The real cause for Stieglitz's December note was his desire to hold the field of catalysis for himself and to get all possible credit for clearing up the large number of important problems in this field. This desire is so great that it lead Stieglitz to make *false charges* against me in December, and now leads him to *depreciate unjustly* the work of others, in order that he may get all the more credit. The field is large enough for the several workers, Kastle, Bredig, Euler, Goldschmidt, Lapworth, Acree, Stieglitz and others, and Stieglitz has no claim over them. I have been working on catalytic phenomena since 1899, especially on problems in tautomerism.[2] I shall endeavor to avoid a conflict with the specific problems of others, unless these problems are a legitimate part of our work. I shall always try to credit others for their work, a thing which Stieglitz has not done.

I wish to have it understood that my reply of January was most emphatically not a "tu quoque" but a "tu solus" answer. If Stieglitz had shown any kind of decent consideration in 1904, or in our correspondence of last summer, for my work and ideas and those of others, we should not now be engaged in this controversy; it was his selfish attitude that made it necessary for me to discuss in detail in my September and December articles the ideas of all the principal workers in catalysis, including Stieglitz; it was his continuation of this attitude in his December note and in his correspondence that made me enter my vigorous protest in January.

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[1] THIS JOURNAL, **39**, 215 (1908).

[2] The ideas involved in the hydrolysis of alkyl halides, of the urazole O-esters by acids, in the catalytic change of O-esters of urazoles, amides, etc., into the N-esters by alkyl halides, in the study of the action of various salts on the alkylation reactions and in other problems in catalytic condensations by alcoholates and alkalies, have been an *absolutely essential part of our work on tautomerism*, as is shown in Brunel's Dissertation, 1906; THIS JOURNAL, **37**, 71; **38**, 1; **38**, 259, 335–348, **39**, 226; and in two articles soon to appear in THIS JOURNAL.

I charged Stieglitz then, as I do now again, with having *deliberately misrepresented* the facts in his December note[1] and in this last reply in his attempt to cast reflections on my honesty and rob me of credit for new and independent ideas in catalysis and especially of priority over him in the theoretical and experimental proof that the second and third "so-called" laws of catalysis do not always hold, and I claim now again that no honorable chemist would have ignored, as did Stieglitz, the work of Kastle,[2] Euler,[3] Bredig,[4] Lapworth,[5] and myself.[6]

The work of these chemists, *together*,[7] anticipated practically all of the ideas put forward by Stieglitz in 1904. Stieglitz should have pointed out the good and bad points in 1904, as I did in my September article and as Stieglitz has now been forced to do by my arraignment of his methods. He chose, instead, in 1904, and in December and now again, to ignore, hide or misrepresent the work of others, and make it appear that he alone is responsible for the recent important developments in catalysis. I use the words "ignore, hide or misrepresent" advisedly because Mr. Stieglitz repeatedly fails again in his last article to credit others with priority in matters which he presents as new and tries to lead his readers to believe that certain theories of catalysis are contrary to the truth.

[1] This Journal, **38**, 743.

[2] *Ibid.*, **19**, 894. Especially see P. Am. Assn. Adv. Sci., **47**, 238, for an abstract of the original article, which was never published in full, and which Prof. Kastle kindly sent me at my request.

[3] Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356; Z. physiol. Chem., **52**, 146.

[4] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528.

[5] Mellor's "Statics and Dynamics," p. 289.

[6] Acree and Hinkins: This Journal, **28**, 370. See also *Ibid.*, **37**, 410; **38**, 258, 489, 746; **39**, 145, 226, 300.

[7] In Professor Acree's original manuscript of his January article the sentence on page 151, last two lines, read: "We see then that Kastle, Euler, Acree and Bredig together had priority over Mr. Stieglitz, etc." The word "*together*" was changed to "*all*" through an error of the assistant editor.—Editor.

Mr. Stieglitz's statement that I proclaimed Kastle as "the original discoverer of the theory of oxonium salts" is not correct. I invite all chemists to read the pp. 147, 149, 156, cited by Stieglitz, and also to read THIS JOURNAL, **38,** 298, 335–339, to learn the truth. Kastle (1898) deserves credit for priority over Collie and Tickle (1899) and Baeyer and Villiger (1901) for the idea that ester hydrochlorides are tetravalent-oxygen compounds, but not for the idea of their ionization. I inserted the words "Kastle's salt" to make it clear to my readers that we call these ester hydrochlorides, today, following Collie and Tickle, *salts.* Although Kastle did not call the ester hydrochlorides *salts* he did call the amide hydrochlorides *salts*[1] and pointed out that the hydrolysis of amides and esters[2] is "essentially the same in kind." We see then that *Kastle preceded Stieglitz just six years* in proposing the views that the catalysis of amides ("nitrogen compounds" analogous to imidoesters) is due to the hydrolysis of the *amide salt,* which has the ammonium-salt structure of Stieglitz's *imidoester salts.* Kastle did not take up the question whether these salts undergo changes through their molecules or ions.

Furthermore, Mr. Stieglitz has deliberately misled his readers concerning Kastle's theory (1) by quoting only from a paper of 1896, after I had quoted Kastle's 1898 paper, *the only one presenting his views fully on catalysis,* and (2) by deliberately making postulations and perversions of the facts and spirit of Kastle's theory, of my 1902 work, by making a mistake in Lapworth's work, etc. I shall point out these and many other errors in my next article on the *Theories of Catalysis,* in which I shall try to deal more fairly with the work and ideas of my various colleagues than Mr. Stieglitz has done.

Mr. Stieglitz, in discussing my work of 1902, has wasted much valuable space in asking a question,[1] "Why was this effort made to force the term *salt* in this sense into his views against the printed evidence?" and in giving himself an answer that pleases him. The real answer, "obvious to every man of even an average intelligence who can read English" (p. 408), is given by the *printed evidence*, my equations,[2] which show that I assumed the compound enz. $C_6H_{11}O_5Ac$ to *ionize* as a *salt* into enz. $C_6H_{11}O_5$ and Ac, and the compound enz. $C_6H_{11}O_5(OH)$ as a *base*[3] into enz. $C_6H_{11}O_5$ and OH:

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[1] His exact words are: "In the catalysis of nitrogen compounds it is only necessary to assume the usual change of valence from three to five....... The amides of the carbonic acids, as is well known, are readily transformed into ammonium salts under the influence of acids; and for reasons similar to those already discussed for the hydrolysis of ethers. A few unstable salts of these amides have been isolated which are of just such a nature as is demanded by the hypothesis, etc., etc." (Manuscript, pp. 19. 21.)

[2] THIS JOURNAL, **39,** 147.

$$\begin{aligned} &C_6H_{11}O_5OH + HAc + \text{enz.} \rightleftarrows \\ &\qquad \text{enz. } C_6H_{11}O_5OH + H + Ac \rightleftarrows \\ &\qquad\qquad \text{enz. } C_6H_{11}O_5 + OH + H + Ac \rightleftarrows \\ &\qquad\qquad\qquad \text{enz. } C_6H_{11}O_5Ac + H_2O \rightleftarrows \\ &\qquad\qquad\qquad\qquad C_6H_{11}O_5Ac + \text{enz.} + H_2O. \end{aligned}$$

Can anything be plainer? I had no occasion to call them *salts* or *bases* in 1902, as Stieglitz was not then *haggling over words*. I believe that my readers see that the *idea* of "acceleration through salt and ion formation" is the central one of my equations of 1902, and that was what I wished to show in January. I shall discuss this in detail in my next article on the *Theories of Catalysis*.

Mr. Stieglitz now tries by *deliberate misquotation* to make it appear that I misquoted him in giving his fundamental points. I only wish that the readers would look through our original papers to see how flagrantly Mr. Stieglitz *misrepresents* me in these quotations. I give his version of my words and my real sentences in parallel columns:

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[1] This Journal, **38**, 406.

[2] *Ibid.*, **28**, 372.

[3] By an oversight this substance was called "enzyme-glucose *salt*" in January (p. 149).

(*a*) Mr. Stieglitz's quotation from me (p. 409): "Mr. Acree's version (claiming to give my fundamental principles: *vide* the original, THIS JOURNAL, **39**, 146, for the exact phraseology): 'Mr. Stieglitz says (p. 744): "In that address, the first vital and decisive step was taken to depart from the old idea that.... the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components......" ' "

My (Acree's) real quotation, giving, as I see them, the fundamental principles worked on by Stieglitz: see THIS JOURNAL, **39**, 146. "Mr. Stieglitz says (p. 744): 'In that address the first vital and decisive step was taken to depart from the old idea that .... the catalytic agent must appear to act by its presence simply and not to form a compound in any quantity with any of the components. ...... The most fundamental fact concerning acids was recalled, the fact that they have the power to form salts with bases and oxides. .... We .... could *prove our point that the acceleration is .... due to salt and ion formation.*' "

Bearing in mind that I was discussing the first "so-called" law of catalysis I leave it to my readers to judge whether I give in the above paragraph (*a*) and in his quotation (*b*) the essence of Mr. Stieglitz's ideas of 1904, on page 744; these, and not his (*my!*) ideas of December, 1907, or later, were the ones under discussion.

In his section (*c*), p. 410, he *deliberately misrepresents* the issue between us. By giving the following sentence of my section (*b*) he makes it appear that I wished to commit him as holding, in December, 1907, the view that the second and third laws of catalysis always hold. *I made there* (p. 153, January) *the crucial point that he did not have in 1904 the views that these laws do not always hold.* Of course, he knew, in December, 1907, that the second and third laws do not always hold because I had published these facts in THIS JOURNAL in April and September, 1907, and had written Stieglitz of the work, and Abel[1] and Euler[2] had reached the same conclusions from theoretical grounds.

[1] Z. Elek. Chem., **13**, 555.

[2] Z. physiol. Chem., **52**, 146.

(*b*) Stieglitz's ideas which appeared, *not in 1904*, but in December, 1907, after he had read my work of September, 1907, given in the opposite column: "...... *in the case of very weak bases*, like methyl acetate, *when the amount of salt formation lies beyond the scope of our methods of experimental measurement*. For all other cases, the three fundamental principles consequently do not apply and in *no case* do they apply rigorously."

My words of September, 1907, of which Stieglitz's ideas in the opposite column, published *later* in December, 1907, look very much like a copy. Page 311: In comparing esterification and oxime hydrolysis: "In this reaction (esterification)[1] the *equilibrium is not disturbed appreciably*"[2] because[1] "little of the hydrogen ions unites with either organic acid or ester, whereas ..... nearly all the hydroxylamine exists in the form of cations." (*And the equilibrium is disturbed.*)[1] Again, on page 349: "These so-called laws are not laws at all, but apply only to certain special cases....." They cannot be used to make predictions concerning all catalytic reactions, but *are only approximate*[2] expressions of special reactions." Again on page 351: "It (the second law)[1] can only hold in those cases in which the base is so weak that *only a trace of the salt is formed*[2]....." Examples could be multiplied.

Mr. Stieglitz's repeated attempts in this last article to take credit from me by stating that he discarded the second and third laws in 1904 only show to what methods he will go to try to get a little more credit for himself; we notice that he never gives a direct quotation to bolster up his position. I invite every one to read his St. Louis paper for himself to see if I am too severe on him.

When now forced to do so by my arraignment, Mr. Stieglitz furnishes the necessary proof of the correctness of my charges that the vital points in his 1904 paper and December note were not new, although he tries to hide his culpability by berating me in the same breath. In his 1904 paper he uses exactly the same formulas for the *intermediate*[1] ester and acid hydrochlorides and hydroxides that Kastle used in 1898. This idea of an intermediate compound, formed by the union of the catalyzing acid, base, etc., and the substance undergoing transformation, is the *vital idea* of catalysis, and one that Euler, Lapworth, Goldschmidt, Bredig, Acree and Stieglitz have also used.

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[1] Words inserted and left out for clearness and conciseness only: see the original.

[2] Italics are new for emphasis.

Furthermore, Mr. Stieglitz now admits (p. 415) that "I (Stieglitz)[2] have never claimed that I was the inventor of the principle that *catalytic action is due to the formation of salts and their ionization*,[3] a principle that was most clearly and emphatically enunciated by Euler in 1901 as a hypothesis, without rigorous experimental proof, although with very good arguments." In other words, Acree was correct in pointing out in January (p. 146) that "Stieglitz's keynote, acceleration through salt and ion formation," was not original with him and is the same keynote that several others are using!

But Mr. Stieglitz did make himself appear to be "the inventor" of this "principle" by not referring to Euler in this connection in his 1904 paper, and thus failing to credit Euler with priority. It is this habit of hiding or ignoring the work of others for which I arraign Stieglitz. Since Stieglitz also gives priority to Euler and others for his (?) (Stieglitz's) (p. 418) ideas as to why the salts of weaker bases change into salts of stronger bases,[4] we see, as I claimed in January, that there is really not very much *new* in Stieglitz's *ideas*: his recently published experimental work, however, showing that imidoester cations are hydrolyzed, and *verifying Bredig's ideas*, is brilliant and that is really all for which he deserves credit.

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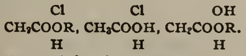
[1] 

$\mathrm{CH_3\overset{Cl}{\underset{H}{C}}OOR,\ CH_3\overset{Cl}{\underset{H}{C}}OOH,\ CH_3\overset{OH}{\underset{H}{C}}OOR.}$

[2] My word, for clearness only.

[3] Italics are mine, for clearness.

[4] That this is not a general rule is shown by the fact that in our oxime and hydrazone work the salt of a strong base, hydroxylamine, or phenylhydrazine, is changed into a salt of a very much weaker base, acetoxime, or acetonephenylhydrazone.

Mr. Stieglitz now confesses that the views of Bredig and Goldschmidt are correct (pp. 414, 415, 425). His excuse that he did not refer to Bredig's complex-cation hypothesis, practically identical with the one used by Stieglitz, myself, Goldschmidt and others "only on account of its being hidden in papers on different topics" is *strange* in view of the fact that the title of Bredig's paper was "Die Jodionen-Katalyse des Wasserstoffsuperoxyds." It was certainly a paper on catalysis, which all workers in catalysis should have read. Besides this I wrote Stieglitz all about these various pieces of work last summer and he read my *September* article, and yet he did not refer to Bredig in this connection in *December*, *January* or *February*. This only shows that even after Stieglitz knows of the prior work of others he fails to give them due credit until forced to do so by some such arraignment as my January article.

Even though Stieglitz cannot see, *after Bredig and Walton pointed it out*, the connection between ester catalysis and their quantitative proof of the catalysis of hydrogen peroxide by iodides *through the intermediate formation and decomposition of an iodoso ion*, some of us can; perhaps Mr. Stieglitz will be *willing* to do so in time. My chief reason for quoting this work in January was simply to show that Stieglitz's imido-ester-cation hydrolysis had been *preceded* by Bredig and Walton's proof of an analogous catalytic reaction through the formation of an intermediate *iodoso anion*, which work led them to postulate the theory of catalysis now used by Stieglitz, Goldschmidt, myself and others.

Mr. Stieglitz's most shameful misrepresentation is his sporadic attempt in his December note and in this last article to make it appear that my work on catalysis and my new ideas are simply a variation and *copy* of his own. Such an assumption is not only absurd but a "fabrication out of the whole cloth."

The equations and ideas used in my September and other articles are simply an expression of the mass law which I have used for several years in my work on tautomerism, reactions of alkyl halides, etc. *These equations did not originate with Stieglitz, but with Guldberg and Waage, and others, about forty years ago!*

I shall now, much against my will, point out some *absurd mistakes* which Mr. Stieglitz made in his St. Louis paper *in the very fundamental mass law and theory of ionization that he parades as the basis of all his work*, mistakes so great that if any one tried to copy them he would be led far away from the new things which I developed. On p. 279, in discussing the catalysis of imidoester hydrochlorides he says: "As the experiments were carried out in dilute solutions in which *the salts are practically completely ionized, it is obvious that it is the positive ion which is decomposing*[1] . . . . . ." This is the evidence then given to us in 1904 to show that imidoester cations, and not the nonionized salt, are hydrolyzed! There is absolutely no word showing that he proved this beyond doubt by changing the relative concentrations of the imidoester cations and the undissociated salt by diluting the solution, or by suppressing the ionization with ammonium chloride, etc., and thus showing that *the mere trace of undissociated salt is not* the substance *hydrolyzed.* To point out to us now that this proved in 1904 that imidoester cations are hydrolyzed is too much for a shrewd man like Stieglitz to ask of us. How could I *copy* this kind of mistake and ever come to my *new* work showing that *it is the very trace of the undissociated hydrochloride of acetylchloraminobenzene that is decomposing*? How could I *copy* such mistakes and ever come to our proof that when alkyl halides react with the practically undissociated urazole acids *only the trace of urazole anions is concerned* to any extent? When I wrote to Mr. Stieglitz last fall about this mistake he assured me that he had carried out in 1904 the experiments I mentioned above. Then why did he not say so in 1904 in his paper? And knowing that I pointed out this mistake to him why does he *deliberately misrepresent* me in December and say that I copied from him, when he knows that I *corrected him*?

And then on p. 282 he has made a mistake[2] in Arrhenius' hydrolysis equation:

$$(Posit.\ Ester\ Ion) = \frac{K_{Base}}{K'} \times (Ester - y) \times (H').$$

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[1] Italics are mine for emphasis.

[2] In his January article (p. 36) he does not make this mistake.

How can H' of hydrogen ions form y of salt without becoming $(H'—y)$, just as *Ester* becomes $(Ester—y)$? How can an acid neutralize a base and yet not change its concentration? Again I ask how can any one *copy* such mistakes and ideas and ever arrive at the absolutely new theoretical and experimental proof that, much of the H' being used up and $(H'—y)$ becoming small in comparison with H', the second and third laws of catalysis do not hold in such cases as the oxime work?

In view of his many mistakes in testing the theories of others, in view of his mistakes in the indicator work,[1] in view of the above mistakes in the fundamental points of his own work, in view of the fact that as late as 1904 he knew so little of calculus that he found it necessary to ask a colleague[2] to solve an equation so simple that the solution is given in Pierce's "Table of Integrals," used by Junior college students, it is evident that any one attempting to copy Stieglitz's immature ideas of 1904 and later would have been led into a hopeless mire and would never have discovered the new points brought out by me.

Still more questionable was Mr. Stieglitz's attempt in December to mislead an innocent chemical public, very few of whom can, or will, follow accurately this complicated question, into believing that "there is not one single new principle in Acree's paper." *The only things[3] that I claimed as new were the two new theoretical and experimental proofs that the second and third laws of catalysis do not always hold*, and, as I pointed out in January, Stieglitz had published, before my April and September articles, *nothing* bearing on this but that the second and third laws *do hold* in esterification work. I pointed out in January that Abel and Euler also have credit with me for these views. But Stieglitz did not point them out in 1904, and his attempt to rob me of these is still more astounding in the light of his January and February articles, in which practically all that he knows, *printed in two*

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[1] See the next article in This Journal.

[2] This Journal, **31**, 463.

[3] *Ibid.*, **38**. 299, 300, 301, especially 335, 339, 342; and *Ibid.*, **39**, 152.

short paragraphs on pp. 56 and 62, is that the second and third laws do not always hold: *and this was written after he knew of my work showing that they do not hold.*

When forced to do so, Mr. Stieglitz now admits (p. 403) "as a welcome addition" my proof that in the rearrangement of acetylchloraminobenzene in the presence of hydrochloric acid we have a case of *pure catalysis* in which the second law does not hold, the velocity being proportional to the concentration of an undissociated salt and to the second power of the concentration of the hydrogen ions instead of to the first power as in esterification, etc. *In a footnote* (p. 412) he now calls my "second proof" of the nonvalidity of the second and third laws "very pretty." How can this "welcome addition" then be a copy of Stieglitz's work when he has done absolutely nothing like it, all of his reactions being those of ions or a free base? Mr. Stieglitz calls this "welcome addition" a "minor" case. Since it is analogous to the catalytic changes of phenylnitramine, phenylnitrosamine, phenylhydroxylamine, phenylsulphaminic acid, diacylanilides, the semidine and benzidine rearrangements, the change of diazoaminobenzene into aminoazobenzene, the catalytic change of alkylanilines into the ring-substituted isomers, the change of alkylpyridinium halides into α-alkylpyridines, the change of phenylpyrazoleiodomethylate into phenylmethylpyrazole, etc., etc., we see that Mr. Stieglitz is still playing the work of others in a "minor chord" in order to make a "major chord" of his own. His statement that he "overlooked" this work (p. 402) is *remarkable* in view of the fact that he admitted to me last September that this was a new principle. It is *impossible* that he could have "overlooked" the 35 and more pages bearing on this particular work in my April and September articles, which he has read[1] and cited, or "overlooked" the constant use on pp. 261, 303, 306, 339, 347 and 493 of this principle in my proof that the undissociated salts of amides, esters and cane sugar, etc., *are not* the particular substances chiefly *undergoing transformation.*

Another misrepresentation, against which I vigorously protest, is Mr. Stieglitz's discussion of my proof that in the oxime work the second and third laws of catalysis do not hold, and that there is a change in equilibrium. *How can this work*

[1] His *misrepresentation* of the facts *3 months later* proves his *guilt.*

be a copy of any of Stieglitz's work when he has done absolutely nothing on reversible reactions? He tries to hide my priority in these new ideas by exclaiming that (p. 411) any "investigator in the field could have told him that" and (p. 410) "no one ever claimed they should" hold, but we notice that he fails to give any references to show that he or any one else ever *thought* of the matter. The obvious fact is that no one ever presented the idea or discussed, before Abel, Euler and I took up the matter *for the first time*, whether they should or should not hold in such cases. And especially amusing and inconsistent is his long *tirade* to the effect that my work on the oximes violates the *old definitions of catalysis* because I have appreciable amounts of salts formed. Yet Mr. Stieglitz heads his papers "Catalysis of Imidoesters," and takes up the study of these imidoesters just because they do form well-defined salts! He *very carefully* "overlooks" the fact that, as a result of our work on catalysis, I have already (September, pp. 348–355; February, pp. 300–309) pointed out that the *old definitions* no longer hold, and that I have broadened them to include such new cases.

Stieglitz's comparison of the change of equilibrium in the oximes with the action of alkalies on a mixture of acid, alcohol, ester and water (*acids*, NOT ALKALIES, *bring about this reversible catalytic reaction!*) brands him as *guilty*[1] either of the grossest ignorance of the application of the mass law, or of deliberate misrepresentation of my work. In his example some of the organic acid is neutralized and absolutely removed from participation in the equilibrium, because the alkali salt formed could not possibly react with the alcohol and form an ester. Hence the apparent equilibrium between the *original* amount of acid, alcohol, water and ester would be disturbed, although the *real* equilibrium between the remaining substances would not. But in the oxime work the addition of more acid *increases* the reacting substances, no one of the reacting constituents is thrown out of the equilibrium reaction in the least, and yet the equilibrium is greatly changed by change in the concentration of the catalyzing acid for the reasons given in September[1] and February.[2] To illustrate with our simplest case, the same equilibrium point is obtained whether we start with acetoxime, water and one equivalent of acid, or with acetone, hydroxylamine and one equivalent of acid: the addition of more acid then changes the equilibrium point. The following scheme represents briefly the equilibrium, as far as we know at present, but the change of equilibrium is independent of the question whether the reaction is that of the cation or undissociated salt:

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[1] I challenge Mr. Stieglitz to give *even one* reference to prove his statement that (p. 411) "$CH_3C(ONa)(OH)(OR)$ is generally considered to be an intermediate product" in the hydrolysis of esters, amides, etc., by alkalies. I brought this out *the first time* in September and Mr. Stieglitz has "overlooked" this fact. I proved then (p. 344) that the *anions* of such salts decompose.

$$(CH_3)_2CO + \overset{+}{N}H_3OH + \overset{-}{Cl} \rightleftarrows$$
$$(CH_3)_2C{=}\overset{+}{N}HOH + \overset{-}{Cl} + H_2O \rightleftarrows$$
$$(CH_3)_2C{=}NOH + \overset{+}{H} + \overset{-}{Cl} + H_2O.$$

Our work and that of Lapworth[3] shows that when less than one equivalent of acid is used the equilibrium is still further changed, and that at least two other reactions set in.

Mr. Stieglitz showed very plainly in our correspondence of last summer that he intended to ignore me and the other workers in catalysis, and "read my new work into his 1904 paper." All that I cared to do in September and January was to point out that Stieglitz's ideas of 1904 were not new, were already public property, and that Stieglitz had used them without proper acknowledgment, whereas I gave all of my colleagues full credit for their ideas in September and January, and included Stieglitz's imidoester-cation hydrolysis. Through his use of Kastle's idea of the intermediate union of the catalyzing acid and the ester, amide, etc.; through his acknowledgment that Bredig's ideas (1903) of ester-cation and sugar-cation hydrolysis are correct; through the fact that Lapworth (1904) showed that ester and acid cations are hydrolyzed or alcoholized; to all of whom I gave *full credit*;[4] and especially through his mistakes in his St. Louis paper

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[1] THIS JOURNAL, **38**, 309, 349, etc.

[2] *Ibid.*, **39**, 400.

[3] J. Chem. Soc., **93**, 85.

[4] That I did give *full credit* is shown, I believe, by the fact that in a recent article (Ber. d. chem. Ges., **41**, 755) Bredig speaks of the idea of *intermediate compounds* "das schon in vielfachen anderen Fällen bei der Katalyse angenommen und nachgewiesen wurde" and then says (footnote) "Literatur siehe bei Acree, l. c."

in the very mass law that he tried to use, Mr. Stieglitz's absurd claim in December that I got from him *my ideas, absolutely different from anything he has done,* not only falls, therefore, but in doing so brings him down in his guilt of having misrepresented me, of having tried to "appropriate" my new ideas, and of having presented his ideas without proper acknowledgment to others.

Once the idea of the formation of any kind of intermediate compound is given, as Kastle did in 1898, Acree in 1902, Bredig in 1903, Lapworth in 1904, etc., it becomes a question of experimental and mathematical detail to determine whether an undissociated salt,[1] a cation,[2] an anion[3] or a neutral molecule[4] is the substance undergoing transformation. I made it perfectly clear to my readers in my September article in my *General Discussion* (p. 297) and the discussion of reversible reactions (p. 334) that the above ideas had already been advanced by (pp. 299, 300, 301, 342) Bredig, Lapworth, Euler, Goldschmidt, Stieglitz, Acree, and then I gave Acree and Johnson's new work and new ideas (pp. 342–355).

Mr. Stieglitz knows only too well that his keynote is, as I pointed out in January, the same keynote that all the rest of us use. He knows only too well that in all physico-organic work, we all use the same mass law, which did not originate with Stieglitz; *that catalytic reactions are at bottom not different from any other reactions*; *that all the results depend upon the constants expressing the formation and reactions of the reacting constituents*; that this can be the only basis of quantitative experimental attack; and that every other chemist must therefore use the same principles.

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[1] Acree and Johnson's rearrangement of acetylchloraminobenzene, and probably the analogous changes of phenylhydroxylamine, phenylnitramine, phenylsulphaminic acid, the semidine rearrangement, etc., etc.

[2] Bredig and Lapworth's ester, sugar, acid, etc., cations; Stieglitz's imidoester cations; Acree and Johnson's acetoxime and hydroxylamine cations; etc.

[3] Acree and Johnson's and Lapworth's work on hydroxylamine anions; Bredig's and Lapworth's work on complex benzaldehyde-cyanide anions; Bredig's catalysis of hydrogen peroxide by an iodoso anion; Acree's work on the action of urazole and other anions on alkyl halides; etc.

[4] Stieglitz and Upson's and Auwer's work on the rearrangement of aminophenylalkyl carbonates, and similar cases; Acree and Johnson's and Lapworth's work on the union of acetone and hydroxylamine.

Johnson and I showed experimentally *for the first time* that the question whether the second or third law holds varies widely with the different experimental problems. Stieglitz has, wilfully or otherwise, missed the point of our work on acetylchloraminobenzene, which was done to prove that even in this case of *pure catalysis*, in which the amount of salt is inappreciably small, the second law of catalysis does not hold. He has missed the whole point of our oxime work, wilfully or otherwise, which was done purely to prove that in the cases in which the salt formation is appreciably large, cases which do violate the old definition of catalysis, the second and third so-called laws do not hold, but yet the mechanism of the catalysis is the same as in some other cases. In other words, I feel with Euler, Abel, Bredig and Bodenstein, that *there is no sharp dividing line* between the cases of *pure catalysis*, in which the amount of intermediate compound formed is inappreciable, and those cases of *pseudo-catalysis* in which the concentration of the intermediate products is comparatively large and the catalyzer is used up in forming the end products. I pointed out in my September paper, on p. 349, in discussing the three so-called laws of catalysis, that "these laws are not laws at all but apply only to certain special cases," that "they cannot be used to make predictions concerning all catalytic reactions, but are only approximate expressions of special reactions," and that "there are two classes of reaction that must be considered in showing that these laws for catalysis by acids (or bases) do not hold," etc., etc. All of these ideas were made perfectly clear in my definition of a catalyzer on pp. 259, 348–355 and also in an article in THIS JOURNAL, 39, 308.

I do not propose to spend any more time in correcting the mistakes and *deliberate misrepresentations* of Mr. Stieglitz.[1]

JOHNS HOPKINS UNIVERSITY,
March 12, 1908.

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[1] I went to Chicago in 1905 primarily to assist two of my students, Mr. Stine and Mr. Holmes, in their organic preparations and to get Mr. Stine started on a dissertation. Prof. J. C. Hessler and Dr. Stine will corroborate me in the statement that I directed Dr. Stine in the study of the bromination of acylanilides. I went there, furthermore, to continue the researches on tautomerism which I was directing in Johns Hopkins University, and I took with me from Baltimore many of my urazoles, etc. Mr. Stieglitz had published some wrong ideas on tautomerism in his paper on indicators,

ON THE THEORY OF INDICATORS AND THE REACTIONS OF PHTHALEINS AND THEIR SALTS.

see errata p. 823

By S. F. Acree. and Julius Stieglitz

(We are being aided in our work on tautomerism by grants from the Carnegie Institution of Washington.)

I wish, as a preface to this article, to *lay especial emphasis* on the fact that, in answer to my statement[1] that he (Mr. Stieglitz) "had expressed 'wrong ideas' in an article on the theory of indicators"[2] Mr. Stieglitz *commits himself now in March, 1908*, as still believing his ideas of 1903 to be essentially correct. He does this by stating that "the (Acree's)[2] allegation was not true, the wrong ideas being wholly the creation of Mr. Acree's imagination."[3] The ideas in the following article, ideas partly mine, partly those of others, show that Mr. Stieglitz's wrong ideas were many more than those indicated in his sentence 'the wrong ideas' were that I (Stieglitz)[2] had overlooked the ionization and salt formation of the phenol groups in the phenolphthalein reactions."[2]

I lay emphasis on this point because Mr. Stieglitz tried in December to "appropriate" my new ideas in catalysis and misrepresented me in regard to a conversation of 1905, and I wish to forestall any chance for him to "discover" that any of the ideas in the following article were presented by him in 1903 or

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and, when I arrived in Chicago, I invited Mr. Stieglitz to collaborate with me on tautomerism, each to furnish his own ideas and methods, just as Slimmer and Stieglitz had done (*vide* Slimmer and Stieglitz: This Journal, **31**, 661). Mr. Stieglitz told me that he was too busy to take up any further work. I do not wish it to be understood from my January article that I told Mr. Stieglitz any of my ideas on tautomeric salts or indicators, or pointed out to him his mistakes in his article on indicators. Naturally, when he told me that he could not join me, I did not care to discuss my ideas with him. I do not believe that we conversed 10 minutes at that time. I make this statement because Mr. Stieglitz misinterpreted, perhaps unconsciously, my sentence (p. 428): "While there I invited Mr. Stieglitz to collaborate with me (on tautomerism and *not* on catalysis) for our mutual benefit, as he had published a paper on tautomeric, compounds in which some wrong ideas were advanced." The clause "as he had published, etc." was intended by me to express *why* I thought of collaborating with Stieglitz, and is not to be interpreted as meaning that I pointed out his mistakes. Mr. Stieglitz has now stated that his wrong ideas are a "creation of Mr. Acree's imagination." I now leave it to my readers to determine whether my criticism of Mr. Stieglitz's views, found in the succeeding article, is just.

[1] This Journal, **37**, 72; **39**, 155.

[2] The words are mine for emphasis.

[3] Mr. Stieglitz's words: This Journal, **39**, 429.

in our conversation of September, 1907. Since I gave him this chance in *March, 1907*, to correct any former mistakes of which he was aware, and since he *commits himself* as being still of the opinion that there were no "wrong ideas" in his paper of 1903, I feel at liberty now to discuss the theories of indicators and dyestuffs from the point of view of the most recent contributions to this subject.

In Stieglitz's[1] article on "The Theories of Indicators" the most important new things are his equations, *which are certainly not entirely correct.*[2] By using the work of Bernsthsen, Nietzki and Schroeter, Nietzki and Burckhardt, Hantzsch and others on such tautomeric compounds, Stieglitz came to the conclusion, arrived at years before, that phenolphthalein behaves like a tautomeric compound, and that (p. 1115) "its red salts are the salts of a carboxylic acid, *not a phenol*,[3] and have the constitution

$$(MOOCC_6H_4)(HOC_6H_4)C:C_6H_4:O.$$

The strongly chromophoric quinoid complex $(:C_6H_4:O)$ *gives us an explanation of the production of intense color, which is entirely adequate*[3] in view of the laws governing color in organic compounds." Then, on page 1122, he gives the equation $C_Q \times C_H = K'' \times C_{LH}$, and says (page 1122) "its tendency to produce the *red color* (*the red salt*[1]) is measured by the same constant K''."

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[1] J. Am. Chem. Soc., **25**, 1112.

[2] An idea of considerable merit that Stieglitz has suggested in this indicator work is that of *quinhydrone formation* of which he spoke to me in September, 1907, and which he mentions now (THIS JOURNAL, **39**, p. 431, footnote), *and that is partly wrong.* Briefly, Stieglitz postulated to me that the alkali changes the phenolphthalein into the salt (see below) $(MeOOCC_6H_4)(HOC_6H_4)C:C_6H_4:O$. This, being both a quinone and a phenol, can form a phenoquinone (or quinhydrone) which would, in general, be more deeply colored than the quinone group and *hence be the chief source of colors in these indicators.* This idea, if correct, would account for the fact that the monophenol esters of phenolphthalein, etc., dissolve in alkalies with little color, the basis being that the quinone group and the phenol ester cannot form such colored quinhydrone derivatives (see Wichelhaus: Ber. d. chem. Ges., **12**, 1501; Hesse: Ann. Chem. (Liebig), **200**, 254). *One set of experiments shows that Stieglitz's idea is wrong.* If his idea were correct all aurine derivatives, having the group $C(C_6H_4OH)_2(:C_6H_4:O)$, and therefore forming this quinhydrone, would, by the addition of alkali, either not change in color at all or, if a diphenolate salt were formed, *the color would decrease. As a matter of fact the color increases* VERY GREATLY *exactly because the alkali salt* $—C(C_6H_4OK)(:C_6H_4:O)$ *is formed.* For all the evidence see the discussion below. I concur with Stieglitz in the belief that much of the color of the free aurines, etc. (*but not of their salts!*) is due to the kind of quinhydrone or phenoquinone formation spoken of by him, but I pointed out to him in September that I still was of the opinion that *my idea of tautomeric salts would explain both the color changes and the reactions of these salts.*

[3] Italics are mine for emphasis: see the discussion of these points below.

Both of the above ideas, that of the constitution of the colored salts and the equation expressing the affinity constant of the phenolphthalein and its tendency to form the red salt *are wrong*. I wish to give here a short statement of our results and the ideas which we are using in this laboratory in studying this problem, which prove that the *quinone theory alone is not adequate, that the chief red salt is a phenol salt*, and that Stieglitz's equations and ideas concerning the formation, constitution and reactions of these salts are wrong. I do not discuss this subject here to impugn Stieglitz, who has at no time claimed that his views on tautomerism are to be considered seriously, but to present some ideas on which I have been gathering evidence during several years in my work on tautomerism. I do not claim any special credit for these ideas, as the facts which make them a necessary assumption to any one with an intimate knowledge of the dyestuffs have long been known. I shall discuss here only the acid tautomeric indicators, and these briefly. But the views hold, in the main, just as well for the basic tautomeric dyes and I shall discuss the entire matter later at more length. I should have brought out these ideas some time ago if I had had the quantitative proof of certain tautomeric phenomena.

I pointed out, however, in my first note that I believed that both of the phenol groups are acids, and that the idea of tautomeric salts would explain the color changes and reactions of phenolphthalein salts. As I felt protected by my first note on tautomerism,[2] and as this quantitative work is necessarily slow, and my collaborators, Brunel, Shadinger, Nirdlinger and especially Johnson, have only recently been able to bring the work to the desired certainty, I have desisted from putting forward any *uncertain* ideas lacking in quantitative evidence.

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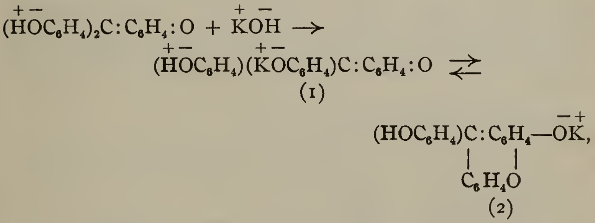
[1] The italics and words in parentheses are mine for emphasis.

[2] This Journal, **37**, 71.

We have shown in this laboratory, and others have added evidence, that the *chief source* of color in such compounds as the salts of aurine, phenolphthalein, etc., is not the quinone complex but the phenol salt of such a quinone compound, which I shall call a *quinonephenolate group*. This colored group may exist in two or more forms, (1) and (2) below, in equilibrium, and the inter- or intramolecular mechanical change from one to the other, or a corresponding movement of electrons, is very probably connected with the color changes. If Stieglitz had only done a little more reading, especially in Friedländer's paper,[1] and those of Nietzki, to which he referred, he would not have made such a mistake. It was at that time well known that solutions of such substances as aurine and rosolic acid,



$$(\overset{+\,-}{HO}C_6H_4)_2C:C_6H_4:O + \overset{+\,-}{KOH} \rightarrow (\overset{+\,-}{HO}C_6H_4)(\overset{+\,-}{KO}C_6H_4)C:C_6H_4:O \rightleftarrows$$

(1)

$$\begin{array}{l}(HOC_6H_4)C:C_6H_4—\overset{-\,+}{OK},\\ \qquad\qquad\quad\ |\qquad\ \ | \\ \qquad\qquad\quad C_6H_4O\end{array}$$

(2)

which already have the quinone complex, become *far*[2] more intensely colored when alkalies are added and the phenol salt is formed. Mr. E. A. Slagle finds that practically colorless solutions of aurine become a deep pink. Nietzki and Burckhardt, to whom Stieglitz referred, showed that the carboxyl ester of tetrabromphenolphthalein,[3]

$$(C_2H_5OOCC_6H_4)(HOC_6H_2Br_2)C:C_6H_2Br_2:O,$$

which already has the quinone complex, gives, in dilute, practically colorless solutions, a blue salt when the phenol group is neutralized by alkalies. But the isomeric phenol ethyl ester, which cannot form a quinonephenolate group, dissolves in alkalies without color.[1] Nietzki and Schroeter,[2] and Mr. Slagle and I, have shown that the fluoresceïn phenol ester, which cannot form the quinonephenolate complex, dissolves in alkalies with very little color, whereas fluoresceïn gives a deep color because it does form such a colored quinonephenolate complex. Likewise, Green and King,[3] and Mr. Slagle and I, have found that the carboxyl esters of phenolphthalein give the same intense color with alkalies that phenolphthalein itself does, because both can form the analogous colored salts,

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[1] Ber. d. chem. Ges., **26**, 172.

[2] See Sutton's "Volumetric Analysis," 1901, p. 38, etc.

[3] Ber. d. chem. Ges., **30**, 177-178.

$$(\mathrm{ROOCC_6H_4})(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{C_6H_4})\mathrm{C:C_6H_4:O}$$

and

$$(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{OCC_6H_4})(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{C_6H_4})\mathrm{C:C_6H_4:O}.$$

But the isomeric phenol methyl ester of phenolphthalein dissolves in alkalies practically without color because it cannot form such a quinonephenolate complex, but gives the salts

$$(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{OCC_6H_4})(\mathrm{CH_3OC_6H_4})\mathrm{C:C_6H_4:O} \rightleftarrows (\mathrm{CH_3OC_6H_4})(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{C_6H_4})\mathrm{C:(OCOC_6H_4)}.$$

Phenolphthalein is useful as an indicator *only* because it forms, not the monobasic salt postulated by Stieglitz,

$$(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{OCC_6H_4})(\mathrm{HOC_6H_4})\mathrm{C:C_6H_4:O},$$

but the dibasic salt

$$(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{OCC_6H_4})(\overset{+}{\mathrm{K}}\overset{-}{\mathrm{O}}\mathrm{C_6H_4})\mathrm{C:C_6H_4:O}.$$

Meyer and Spengler,[4] who were the first to prove experimentally that the colored salts are dibasic salts, were inclined to give these salts the lactoid form. As early as 1893 Friedländer[5] pointed out that the relation of aurine to phenolphthalein leads to the conclusion that the red salts of phenolphthalein must be dibasic salts with the quinone nucleus. The carboxyl ester of phenolphthalein is a better[1] indicator than phenolphthalein itself because it takes only half as much alkali to form the really chromophoric group

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[1] Ber. d. chem. Ges., **30**, 178.

[2] *Ibid.*, **28**, 48.

[3] *Ibid.*, **40**, 3724.

[4] *Ibid.*, **38**, 1318.

[5] *Ibid.*, **26**, 172.

$$RC(C_6H_4\overset{-}{O}\overset{+}{K})(:C_6H_4:O).$$

These ideas account for the fact that Bistrzycki's[2] diphenylquinonemethane,

$$(C_6H_5)_2C:C_6H_4:O,$$

is far less deeply colored than the salts of benzaurine,

$$C_6H_5C(:C_6H_4:O)(C_6H_4\overset{-}{O}\overset{+}{Na}),$$

and aurine,

$$(HOC_6H_4)(\overset{+}{Na}\overset{-}{O}C_6H_4)C:C_6H_4:O.$$

The latter can form the deeply colored quinonephenolate addition product, while the diphenylquinonemethane has no such group. The above ideas and space interference probably explain in part the lack of intense color in the salts of the various dioxy- and diaminotriphenylcarbinols and the corresponding trisubstituted compounds not having the substituent groups in the para positions. Examples of this class could be multiplied.

There is no longer any question that alkalies (acids) tend to cause the quinone group in all such compounds to become hydrated and colorless,[3] perhaps on account of salt formation. This accounts for the fading of the color when phenolphthalein, etc., are treated with an excess of alkali. Green and Perkin showed that the hydrate,

$$(HOC_6H_4)_2C(OH)C_6H_4COONa,$$

loses water only very slowly at lower temperatures.

The constitution of the colored compounds or the cause of the color are still to be cleared up, and it is immaterial for this hypothesis whether the views of Jackson or those of

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[1] Ber. d. chem. Ges., **40**, 3728.

[2] *Ibid.*, **36**, 2337.

[3] Bistrzycki: *Loc. cit.*; Ber. d. chem. Ges., **36**, 3558, 3565. Green and Perkin: J. Chem. Soc., **85**, 398.

Posner[1] are correct. It suffices to say that the idea of the union of the metallic phenolate with the quinone complex, involving perhaps ionization, seems to be the central cause. Evidence for this lies in the fact that Jackson and Oenslager,[2] and also Wichelhaus,[3] have isolated deeply colored salts,

$$C_6H_4(ONa)_2(OC_6H_5)_2, \quad C_6H_4(ONa)_2(\beta\text{-}OC_{10}H_7)_2,$$

etc., which are formed by the union of sodium phenolate, or naphtholate, with quinone, and that Mr. Slagle and I have formed deeply colored compounds by the union of benzoquinone or anthraquinone with salts of *o*-cresol, *p*-cresol, phenol, hydroquinone, pyrogallol and resorcinol, the color of which disappears when acids are added. In fact such mixtures serve as very good indicators.

We suspect, further, that alkaline solutions of pyrogallol, etc., become colored when oxidized merely because some of the pyrogallol gives a quinone which then forms a quinone-phenolate with some of the unchanged alkali salt of the pyrogallol, etc., or with the salt of some of the products of oxidation. When acids are added the color fades just as in the experiments spoken of above.

Exactly the same kind of reasoning applies to the color changes in rosaniline and similar compounds, only in this case the chief colored substance is formed by the union of the quinone group (itself a salt) and a free base, instead of a quinone and salt, as in the aurine and phenolphthalein groups. In the rosaniline series the colorless carbinol, a very weak base, is in equilibrium with a trace of the quinone complex, a much stronger base:

$$\begin{array}{ccc} (NH_2C_6H_4)_3COH & \rightleftarrows & (NH_2C_6H_4)_2C:C_6H_4:NH_2OH \\ \uparrow\downarrow & & \uparrow\downarrow \\ (NH_2C_6H_4)_3\overset{+}{C} + \overset{-}{OH} & & (NH_2C_6H_4)_2C:C_6H_4:\overset{+}{N}H_2 + \overset{-}{OH} \end{array} \Bigg\} \rightleftarrows$$

$$(NH_2C_6H_4)_2C:C_6H_4:\overset{+}{N}H_2\overset{-}{O}H.$$

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[1] Ann. Chem. (Liebig), 336, 85.

[2] THIS JOURNAL, 18, 1.

[3] Ber. d. chem. Ges., 5, 849.

When an equivalent of a stronger acid is added, much salt,

$$(NH_2C_6H_4)_2C:C_6H_4:\overset{+}{N}H_2\overset{-}{Cl},$$

of the stronger base is formed, and incidentally there is a deep color produced. *Now the* CHIEF CAUSE *of this color is not the colored quinone group, as Mr. Stieglitz believed, but the double compound formed by the inter- or intramolecular union of the quinone complex with the free aniline (or aniline hydroxide) groups of the dyestuff.* One of the possible modes of union is shown by the dotted lines in the above equation. In order to show the analogy of these colored compounds to the quinhydrones and phenoquinones we shall call them *quinaminones.* What is the evidence?

Jackson and Clarke[1] showed very clearly that in non-aqueous solutions *o*- and *p*-quinones form deeply colored addition products with aromatic amines, but not with the amine salts. They isolated, for example, the unstable compounds,

$$C_6Br_4O_2.C_6H_5N(CH_3)_2, \quad C_6Cl_4O_2.C_6H_5N(CH_3)_2,$$

etc., which were formed by the *reversible* union of one molecule of dimethylaniline with one molecule each of tetrabromorthoquinone, chloranil, etc. Mr. Slagle and I have been able to show that the same phenomena are exhibited beautifully in aqueous solutions. The addition of an equivalent amount of an aqueous solution of dimethylaniline hydrochloride to one of quinone produces no color change; but when an alkali is added to the solution and the dimethylaniline is liberated, the quinone and amine unite to some extent in a reversible reaction, and the color changes to a brownish red or brownish purple: the addition of an acid removes the amine and hence causes the color to fade to that of the quinone. The addition of an aqueous solution of a salt of α-dimethylamino-α-bromnaphthalene to one of quinone produces no color change. But when an alkali is added gradually and the amine base is liberated, the quinone and amine unite to some extent and form some *quinaminone*, and the color changes successively to yellow, pink and a deep brown. When the solution is acidified and the amine is neutralized the color fades to that of the quinone.

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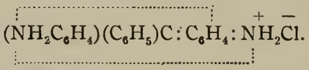
[1] This Journal, 34, 441.

These experiments prove conclusively that quinones form addition products with anilines and naphthylamines (but not with their salts) which are far more deeply colored than the quinones themselves.

The reactions of all the dyestuffs analogous to the rosaniline series prove the same point. Evidence for this *quinaminone* formation is found in a large number of facts similar to the following: *p*-Aminotriphenylcarbinol and acids give only an orange color from the quinone group of the salt

$$(C_6H_5)_2C:C_6H_4:\overset{+}{N}H_2\overset{-}{Cl}.$$

But the *p,p*-diaminotriphenylcarbinol gives an intense violet color because it forms, to some extent, the deeply colored *quinaminone* group in the salt



$$(NH_2C_6H_4)(C_6H_5)C:C_6H_4:\overset{+}{N}H_2\overset{-}{Cl}.$$

Now if the color is due chiefly to the *quinaminone* group instead of the quinone group, the addition of more and more acid should cause a *decrease* in the color because the amine groups would be converted into their salts, which do not unite with the quinone group and form the colored *quinaminone.* The evidence certainly sustains the above hypothesis. The addition of hydrochloric acid to malachite green causes a fading of the color, as the amino group is neutralized, from bluish green to greenish yellow and then to reddish yellow, which is probably the modified color of the quinone group. The addition of alkali causes a reversal of these color changes to the original bluish green, because the quinaminone group is then reformed from the liberated amino group and the quinone. An excess of alkali, of course, converts the salt into the base which then rearranges into the colorless carbinol. The addition of hydrochloric acid to a fuchsine solution causes a change from the intense carmine red to a much less intense reddish yellow, which is probably the color of the quinone group modified by the various auxochromes. When the acid is neutralized the original color is restored. Examples could be multiplied.

The point is that the CHIEF SOURCE *of color in indicators (both basic and acid) and substances of these types is not the quinone group, but one or more*[1] *inter- or intramolecular combinations of a quinone group with a salt of phenol, or with an anilinelike group. A small amount of color is, of course, due to the quinone group because all quinones are somewhat colored.*

I am not alone in differing from some of the views presented by Stieglitz, as Baeyer has recently pointed out some of the above relations in a valuable article[2] on the dyestuffs and Hantzsch has suggested similar ideas to account for the color of his nitrophenol salts, while King and Green think that the colored salts of phthaleins may be hydrated. Baeyer tested the above hypothesis, advanced first by Jackson, by trying to obtain colored solutions by the use of fuchson, or fuchsonimonium chloride, and sodium phenolate, or dimethyl-*p*-toluidine. No colors were obtained and he discarded the quinonephenolate hypothesis in favor of ideas similar to those used by Hartley and by Baly.[3] Our experiments with quinones and phenolates and aromatic amines, however, gave beautiful color reactions, a result not easily explained by the ideas of Hartley and Baly, as applied by Baeyer. As I see it, all of the facts known at present are readily understood when Jackson's ideas and the oscillation hypothesis of Baly are used, and I have given them preference above. We must keep our minds open to the fact that both, and perhaps other explanations, may be concerned in these complicated phenomena, and this communication is to be considered only in that light.

In our quantitative study of these phenomena we shall try to determine all of the quantitative relations between the color intensity and all of the equilibrium and dissociation constants. We shall study the relation between the concentration of the sodium phenoquinonate and of the quinone and the sodium phenolate and its ions,

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[1] Several possibilities present themselves, and these may be the source of the different colors shown in the absorption spectra of these dyestuffs, and exhibited by their solutions under varying conditions of dilution, acidity, alkalinity, temperature, etc.

[2] Ann. Chem. (Liebig), **354**, 162. 152

[3] J. Chem. Soc., **85**, 1029; **89**, 502, 514; **91**, 426, 1572.

$$(1 \text{ or } 2)C_6H_5\overset{-}{O},\overset{+}{Na} + O:C_6H_4:O \rightleftarrows O:C_6H_4:O(1 \text{ or } 2)C_6H_5\overset{-}{O},\overset{+}{Na},$$

and the relation between the concentration of the *quinaminone* and of the quinone and aniline derivatives, etc.:

$$C_6H_5N(CH_3)_2 + O:C_6H_4:O \rightleftarrows O:C_6H_4:O.C_6H_5N(CH_3)_2.$$

We shall study especially the possible relation between the color intensity and the dissociation constants of the phenol salts and quinone salts. This will be done in the simple cases as well as with the tautomeric phthaleins, rosanilines, etc.

It is needless to say, as I pointed out in a former paper,[1] that "there is not sufficient quantitative evidence on hand to enable us to see clearly the mechanism of the reactions involved in the changes from the colorless to the colored substances, or *vice versa*, or to say whether the changes are molecular or ionic, whether they take place directly or through intermediate stages. The ionic theory and the chromophoric theory have such a hold upon us that we attempt to interpret all of the above changes by means of them. They may contain a great deal of truth, but also a great deal that must ultimately be discarded. What we need is a large amount of quantitative work to help us find the truth." For this reason I wish to state that the ideas on tautomerism discussed in the succeeding pages, as well as those in the preceding sections, are based on the results of our rigorous qualitative and quantitative work in the field of tautomerism, and especially with the urazoles.

And now we come to that equation $C_Q \times C_H = K'' \times C_{LH}$ which Stieglitz said gives us the affinity constant of a tautomeric compound like phenolphthalein, or the tendency to produce the red color or red salt.[2] How can any such equation, involving only the dissociation of the carboxyl group, give us the affinity constant of *this tautomeric dibasic acid* in which the carboxyl group and the phenol group *both* give hydrogen ions as follows:

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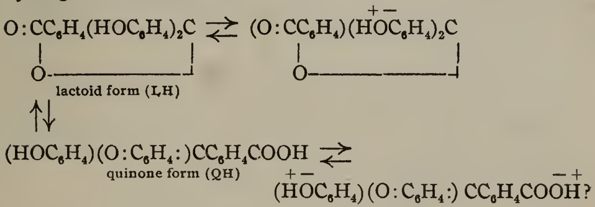
[1] This Journal, 38, 28.

[2] For his development of this equation and the terms used see J. Am. Chem. Soc., 25, page 1122.



$$\underset{\text{lactoid form (LH)}}{\underbrace{O{:}CC_6H_4(HOC_6H_4)_2C}_{O}} \rightleftarrows \underbrace{(O{:}CC_6H_4)(\overset{+\,-}{HO}C_6H_4)_2C}_{O}$$

$$\updownarrow$$

$$\underset{\text{quinone form (QH)}}{(HOC_6H_4)(O{:}C_6H_4{:})CC_6H_4COOH} \rightleftarrows (\overset{+\,-}{HO}C_6H_4)(O{:}C_6H_4{:})\,CC_6H_4CO\overset{-\,+}{OH}?$$

How can any such equation, *expressing only the dissociation of the carboxyl group*, give us the "tendency to form the red color" from the red salt when that red salt is the dibasic *carboxyl* and *phenol* salt? It is perfectly evident that *a formula giving the correct affinity constant must take into consideration the two different tautomeric forms and the extra phenol group*, and a reference to a paper by Acree in This Journal, 38, 1, will show Mr. Stieglitz a large number of such cases worked out. *The ideas discussed in the succeeding pages, as well as those in the preceding pages, are the results of our rigorous experimental work in the field of tautomerism.*

It is further evident that the lactoid and quinoid forms are *weak*[1] dibasic acids and should be called LH_2 and QH_2 since each has two hydrogen atoms replaceable by metals. The carboxyl group of QH_2 is without doubt stronger than the phenol group. The development of the affinity constant of the phenolphthalein must be directly related to the affinity constants K_1 and K'_1 of the lactoid form LH_2, to the affinity constants K_2 and K'_2 of the quinone form QH_2, and to K_3, the equilibrium constant of the two tautomeric forms. I assume that the molecular forms of these acids and salts are in equilibrium because Dimroth[2] and Acree[3] have proved such to be the case with other tautomeric acids and salts and I reserve the right to use our other form of equation when we prove in any case that the anions or cations are in equilibrium.

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[1] McCoy: This Journal, **31**, 503. Salm: Z. physik. Chem., **57**, 471. Veley: *Ibid.*, **57**, 147; **61**, 464. J. Chem. Soc., **91**, 156.

[2] Ann. Chem. (Liebig), **335**, 1; **338**, 143.

[3] This Journal, **37**, 71; **38**, 1.

Now Ostwald,[1] Smith,[2] Noyes[3] and Trevor[4] have shown that such weak dibasic acids obey Ostwald's dilution law. We therefore have

$$C_{LH} \times C_H = K_1C_{LH_2}, C_{QH} \times C_H = K_2C_{QH_2}, \text{and } C_{LH_2} = K_3C_{QH_2}.$$

From this it follows that the affinity constant of the phenolphthalein is represented as accurately as our present experimental methods will show by the equation

$$\frac{(C_{LH} + C_{QH}) \times C_H}{(C_{LH_2} + C_{QH_2})} = \frac{K_2 + K_1K_3}{1 + K_3} = K,$$

which is quite different from Mr. Stieglitz's equation,

$$C_Q \times C_H = K'' \times C_{LH}.$$

That my equations are the correct ones for showing the affinity constants of such weak tautomeric acids was not only developed theoretically by the use of the mass law, but proved experimentally by Acree and Shadinger[5] in the work on a large number of tautomeric urazoles. The equation

$$\frac{H \times (C_{ki} + C'_{ki}, \text{etc.}, + C_{ei} + C'_{ei}, \text{etc.})}{(C_k + C'_k, \text{etc.}, + C_e + C'_e, \text{etc.})} = K,$$

for instance, was shown to hold perfectly well for substances (phenylurazole, etc.) having a large number (four or more) of weakly tautomeric acid forms.

But the tendency to form the red salt or red color is still more complicated than Mr. Stieglitz thought. The moment LHNa and QHNa are formed, they set up, as our work on tautomerism shows, their own equilibrium conditions practically instantaneously, as follows:

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[1] Z. physik. Chem., **3**, 280.

[2] *Ibid.*, **25**, 144, 193.

[3] *Ibid.*, **11**, 495; **13**, 417.

[4] *Ibid.*, **10**, 321.

[5] THIS JOURNAL, **39**, 124. Shadinger: Dissertation, Johns Hopkins Univ., 1907.

$$\underset{(1)}{(O{:}C_6H_4{:})(HOC_6H_4)CC_6H_4COONa} \underset{K'_3}{\rightleftarrows} \underset{(2)}{(HOC_6H_4)(NaOC_6H_4)C{:}(OCOC_6H_4)} \underset{K''_3}{\rightleftarrows} \underset{(3)\ (\text{a trace})}{(NaOC_6H_4)(O{:}C_6H_4{:})CC_6H_4COOH.}$$

Of the three monoalkali salts (1) and (3) give some color but even that is faint in comparison with the color of their corresponding dimetallic salt, QNa_2. (1) and (3) yield directly the colored salt,

$$(\overset{+}{Na}\overset{-}{O}C_6H_4)(O{:}C_6H_4{:})CC_6H_4CO\overset{-}{O}\overset{+}{Na},$$

and (2) yields this colored salt *indirectly* through the tautomeric rearrangement of the dimetallic salt, LNa_2, corresponding to (2).

If we call C_{QHNa} the concentration of (1), C_{LHNa} that of (2), and C_{QNaH} that of (3), and consider that (1) dissociates partly into H and C_{QNa}, while (3) gives H and C'_{QNa}, and recognize the possible ionization of all these, the affinity constant of this tautomeric monosodium salt must be expressed approximately by a complicated equation having *something* of this form, though not exactly,

$$\frac{C_H \times (\bar{C}_{QNa} + \bar{\bar{C}}_Q + \bar{C}_{LNa} + \bar{\bar{C}}_L + \bar{C}'_{QNa},\ \text{etc.})}{(C_{QHNa} + C_{LHNa} + C_{QNaH},\ \text{etc.})} = K,$$

in which K is a very complex function involving the dissociation constants of these acid salts and the equilibrium constants K'_3 and K''_3.

For the total amount of the disodium salt formed the following equilibrium relations would hold for the undissociated portions:

$$\underset{(4)}{(NaOC_6H_4)_2C{:}(OCOC_6H_4)} \rightleftarrows \underset{(5)}{(NaOC_6H_4)(O{:}C_6H_4{:})CC_6H_4COONa} \underset{K_3'''}{\rightleftarrows} \underset{(6)}{(NaOC_6H_4)(O{:}C_6H_4{:})CC_6H_4COONa,}$$

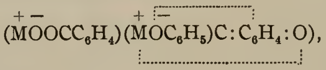
in which K'''_3 is intended merely to express the probable equilibrium between the actual deeply colored salts (6), whatever their nature, and the quinone dibasic salt (5). It is evident then that the color of the phenolphthalein solution is due to some extent to the salts (1), (3) and (5), but *chiefly* to (6), which may exist in several forms. We are investigating the decrease of the color of these salts in alcohols, acetone, etc., from the following points of view: (1) that in these solvents a change of the equilibrium results and much more of the salt (4) is formed; (2) that the quinone group takes up alcohol readily and becomes colorless; and (3) that the salts (4), (5) and (6) are changed in dissociation. When we learn the values of all the above constants we can easily express in numbers the affinity constant of phenolphthalein and its "tendency to give the red color."

The above ideas lead to equations which express the *sensitiveness* of indicators to acids and alkalies, already discussed by Ostwald. These equations are developed in the way already published[1] and will be given in detail in our full report.

Stieglitz's equation above not only fails to give the affinity constant of phenolphthalein, *but does not even show the tendency of the phenolphthalein to give the red salt or the red color.* It fails to do so purely because it gives an approximation of the tendeney to form a salt

$$(\overset{+}{M}\overset{-}{O}OCC_6H_4)(HOC_6H_4)C:C_6H_4:O,$$

which is not the colored salt or salts,



$$(\overset{+}{M}\overset{-}{O}OCC_6H_4)(\overset{+}{M}\overset{-}{O}C_6H_5)C:C_6H_4:O),$$

chiefly concerned.

Not only do the above ideas of tautomeric acids and salts lead us to a clearer understanding of the color changes involved in phenolphthalein, fluoresceïn, etc., but they also make clear the formation of the various esters when the salts of such compounds are treated with alkyl halides. Potassium fluoresceïn and ethyl iodide give the four possible mono- and diethyl esters.[1] Our ideas on such tautomeric salts have been proved *quantitatively*[2] by our work on urazoles and are being extended in several directions. The following formulae will show the outline of the work that we are carrying forward, the validity of which will be tested by quantitative methods. We believe that such formulae represent, at least to a large extent, the constitution of the salts, whose undissociated forms are the ones probably in equilibrium, which in solutions are ionized, which give us the color, and the anions of which yield the esters. We use phenolphthalein merely as an example.

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[1] This Journal, 38, 1.

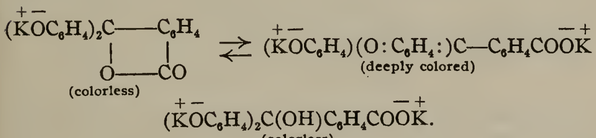
Monobasic salts:

$$\underset{\text{(somewhat colored)}}{(O:C_6H_4:)(\overset{+}{H}\overset{-}{O}C_6H_4)CC_6H_4CO\overset{-}{O}\overset{+}{K}} \rightleftarrows$$

$$\underset{\text{(colorless)}}{(\overset{+}{H}\overset{-}{O}C_6H_4)(\overset{+}{K}\overset{-}{O}C_6H_4)C(OCOC_6H_4)} \rightleftarrows$$

$$\underset{\text{(deeply colored)}}{(\overset{+}{K}\overset{-}{O}C_6H_4)(O:C_6H_4:)CC_6H_4CO\overset{-}{O}\overset{+}{H}}.$$

Dibasic salts:



$$\underset{\text{(colorless)}}{\begin{array}{ccc}(\overset{+}{K}\overset{-}{O}C_6H_4)_2C & \text{——} & C_6H_4\\ | & & |\\ O & \text{——} & CO\end{array}} \rightleftarrows \underset{\text{(deeply colored)}}{(\overset{+}{K}\overset{-}{O}C_6H_4)(O:C_6H_4:)C\text{—}C_6H_4CO\overset{-}{O}\overset{+}{K}}$$

$$\underset{\text{(colorless)}}{(\overset{+}{K}\overset{-}{O}C_6H_4)_2C(OH)C_6H_4CO\overset{-}{O}\overset{+}{K}}.$$

The anions of these tautomeric salts seem to react with the alkyl halides and yield the various tautomeric esters in the manner proved quantitatively for the urazoles.[3] In certain cases some of the esters may rearrange into others, as Meyer[1] has recently found, and as has been shown in the isomeric change of the O-esters of urazoles, oxylepidine, quinazolines, amides, etc., into the corresponding N-esters. We are investigating the reactions of phenolphthalein, fluoresceïn, etc., with alkyl halides, diazomethane, -ethane, etc.

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[1] Ber. d. chem. Ges., **28**, 48.

[2] Acree: This Journal **37**, 71. Acree and Shadinger: *Ibid.*, **39**, 124. Shadinger: Dissertation, Johns Hopkins Univ., 1907. Acree, Brunel, Shadinger, Nirdlinger and Johnson: Article on tautomeric salts read before the Am. Chem. Soc., Jan. 1, 1908.

[3] Brunel: Dissertation, Johns Hopkins Univ., 1906. Acree: This Journal, **37**, 71; **38**, 1. Acree and Shadinger: *Ibid.*, **39**, 226. Acree: Year Book of the Carnegie Institution of Washington, No. 6, p. 178. Acree, Johnson, Brunel, Shadinger and Nirdlinger: An article on tautomerism soon to appear in This Journal.

Johns Hopkins University,
February 20, 1908.

STUDIES IN BROMINATION: A REPLY TO COHEN AND CROSS.[2]

By S. F. Acree, J. M. Johnson and Sidney Nirdlinger.

In answer to the statement of Cohen and Cross that part of our ideas[3] that such compounds as

$$CH_3CONHBr_2C_6H_5$$

are intermediate substances in the formation of the compound

$$CH_3CONBrC_6H_5,$$

etc., and in its catalysis by hydrobromic acid were derived from their work, we wish to point out the following:

(1) Mr. Nirdlinger's notebook[4] shows that his compound,

$$CH_3CON(CH_3)Br_2C_6H_5,$$

analogous to the compound,

$$CH_3CONHBr_2C_6H_4CH_3,$$

of Cohen and Cross, was analyzed on March 9th, 1907, or two months before Cohen and Cross published their paper. We should have mentioned this in April,[5] September[6] and December if we had anticipated any controversy.

(2) On page 272 of our September paper and 747 of our December paper we gave Jackson and Clarke[7] credit for priority in the experimental proof of the idea used by us

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[1] Meyer and Marx: Ber. d. Chem. Ges., **40**, 1437.

[2] This Journal, **39**, 431.

[3] *Ibid.*, **38**, 746.

[4] I have examined the notebook here referred to and I certify that the statement is in accordance with the fact.—Editor.

[5] This Journal, **37**, 410.

[6] *Ibid.*, **38**, 265.

[7] *Ibid.*, **34**, 261; **36**, 409. Fries: Ann. Chem. (Liebig), **346**, 128.

that such a dibrom derivative is an intermediate compound in the strictly analogous reaction:

$$\begin{aligned}(CH_3)_2NC_6H_5 + Br_2 \rightleftarrows (CH_3)_2NBr_2C_6H_5 &\rightarrow \\ (CH_3)_2NHBrC_6H_4Br &\rightleftarrows (CH_3)_2NC_6H_4Br + HBr.\end{aligned}$$

We take pleasure too in stating that Professor K. J. P. Orton has called our attention to the fact that he has advocated this view for some years; his results are to be found in a number of interesting papers[1] on this and related rearrangements.

(3) The equation (1) which Cohen and Cross claim that we wrote in December for the first time is exactly like (2) which is found on page 273 of the September article, Cl simply taking the place of H:

$$\begin{aligned}(1)\ CH_3CONHC_6H_5 + Br_2 \rightleftarrows CH_3CONHBr_2C_6H_5 &\rightarrow \\ CH_3CONHC_6H_4Br &+ HBr;\\ (2)\ CH_3CONClC_6H_5 + Br_2 \rightleftarrows CH_3CONClBr_2C_6H_5 &\rightarrow \\ CH_3CONHC_6H_4Br &+ ClBr.\end{aligned}$$

We do not lay any stress on this, the idea having already been advanced by Jackson and Clarke, and perhaps by others. Our interest in the matter lies chiefly in the quantitative side and in the light that we were able to throw on catalysis.

(4) The equations given by Cohen and Cross[2] are not in harmony with our results:

$$\begin{aligned}CH_3CONHC_7H_7 \rightarrow \underset{\text{A.}}{CH_3CONHBr_2C_7H_7} &\rightarrow \\ \underset{\text{B.}}{CH_3CONBrC_7H_7} &\rightarrow \underset{\text{C.}}{CH_3CONHC_7H_6Br}.\end{aligned}$$

The substance A., not B., is transformed directly into C., as was suggested by Orton, and definitely proved by the work of Jackson and Clarke and by our quantitative investigations.

Our December note was written in no controversial spirit, as we simply wished to point out that we have been engaged intermittently on this problem four years, and especially during the last two years. We are glad to welcome the interesting results of Cohen and Cross, or of any others, in this line of work. We have noticed some apparently abnormal rearrangements in this class of compounds which we shall continue to study.

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[1] J. Chem. Soc., **83**, 796; **87**, 389; **91**, 146, 1543, 1554; and earlier papers.

[2] Chem. News, **95**, 274. Acree, Johnson and Nirdlinger: This Journal, **38**, 747.

JOHNS HOPKINS UNIVERSITY,
March 6, 1908.

REPORTS.

THEORIES OF OSMOTIC PRESSURE.

The Thermodynamic View.

The striking analogies between the osmotic pressure of solutions of cane sugar in water and the elastic pressure of gases, brought out by Pfeffer's work,[1] led van't Hoff to conclude that there is a deep-seated relation between the two sets of phenomena and he accordingly put forward his kinetic theory of solutions,[2] in which the osmotic pressure of dilute solutions is ascribed wholly to the bombardment of the membrane separating solution and solvent by the dissolved molecules, while in the case of more concentrated solutions the mutual attractions of solute and solvent come into play.[3]

He then attacked the problem from the theoretical side. Assuming a perfectly semipermeable membrane, he proved that the osmotic pressure of a dilute solution of a gas is equal in value to the elastic pressure which the solute would exert in the gaseous condition at the same temperature and volume. The solution must be so dilute that the mutual attractions of the dissolved molecules, as also the space actually occupied by them, are negligible. The method of proof is based on the assumption of a thermodynamically passive membrane, that is, one that permits the carrying out of a reversible cycle, and on the application of the second law of thermodynamics. Van't Hoff next passes from solutions of gases to solutions in general and concludes that for "ideal solutions," that is, solutions dilute enough to conform to the conditions named above, the laws of gases must hold.

In the development of the kinetic theory of gases, in its simplest form, the same assumptions with regard to concentration are made as were made by van't Hoff for solutions.

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[1] Osmotische Untersuchungen, Leipzig, 1877.

[2] Z. physik. Chem., 1, 481 (1887).

[3] Address before the British Association at Leeds in 1890.

It is further necessary to assume that the gas molecules move with considerable velocities. The difficulties involved in making these assumptions when we come to deal with solutions have been repeatedly pointed out. Plainly, the case here is much more complicated. In solutions, besides the relatively small number of solute molecules, we have present an enormous number of molecules of solvent, so that even if we could neglect the mutual attraction between solute molecules, that between solute and solvent should probably be taken into account. It is to be noted, however, that the solute molecule is always *completely* surrounded by solvent molecules and hence the resultant of all the forces acting upon it, due to solvent, is zero, and consequently its velocity as it approaches the membrane is not affected, provided the solution is so dilute that we may neglect the difference in concentration of solvent molecules on the two sides of the membrane.

A further difficulty in the way of extension of the kinetic theory to solutions arises from the relatively slow rate of diffusion in liquids as compared with that of gases. With regard to this objection, it has been pointed out that what we are concerned with is not the velocity of diffusion in the ordinary sense. Diffusion velocity is determined by noting the time required by a molecule, for example, to travel through a finite distance, say from A to B, but during this interval the molecule has probably traversed many times this distance, by a zigzag path, experiencing a very large number of encounters with neighboring molecules, both of solute and solvent—a much larger number, probably, than the gas molecule meets with. The straight-line distance A B bears no known relation to the actual velocity of the molecule between successive impacts, and this velocity, which determines the kinetic energy of the particle and with which alone we are concerned, may be comparable with the velocity of the gas molecule.

As indicated above, van't Hoff's deductions were specifically limited to very dilute solutions. This is not surprising, inasmuch as the relation $PV = RT$ holds rigidly for gases only under the very conditions laid down by van't Hoff for solutions. For more concentrated gases van der Waals found it necessary to introduce correction terms for the mutual attractions of the molecules and for the space occupied by them. His equation has the form $\left(P + \frac{a}{V^2}\right)(V-b) = RT$. By their recent work, Morse and

Frazer and their coworkers[1] have greatly extended the range over which the gas laws apparently hold by regarding V in the equation $PV = RT$ as the volume of the *solvent* and not of the *solution.* This is in effect what van der Waals has done for gases, *viz.*, correcting for the space occupied by the molecules of the dissolved substance.

Lord Rayleigh,[2] by an independent though somewhat similar method of thermodynamic reasoning, arrived at the same conclusion formerly reached by van't Hoff as to the numerical identity between theoretical gas and osmotic pressures.

Prof. Larmor,[3] considering the subject in its relation to the general molecular theory, also places osmotic theory on the thermodynamic basis. His treatment is free from the objection urged by Lord Kelvin[4] to the method employed by van't Hoff and Rayleigh. Both these authors base their proofs upon the law of Henry, and Lord Kelvin seems to regard any extension of the theory to cases in which this law does not hold or in which there is a change in molecular aggregation on solution as unwarranted. Prof. Larmor, however, places the theory of osmotic pressure on a purely abstract basis. The laws of solubility of gases or possible change in the state of molecular aggregation during solution are not involved. To quote from him: "The following position is, I think, sound. Each molecule of the dissolved substance forms for itself a *nidus* in the solvent; that is, it sensibly influences the molecules around it up to a certain minute distance so as to form a loosely connected complex in the sense, not of chemical union, but of physical influence. The laws of this mutual molecular influence are unknown, possibly unknowable; but, provided the solution is so dilute that each such complex is for very much the greater part of the time out of range of the influence of the other complexes (as, for instance, are the separate molecules of a free gas), then the principles of thermodynamics necessitate the osmotic laws."

The experiments of Prof. William Ramsay[5] on the passage of hydrogen through a palladium septum, illustrating what has been termed the osmotic pressure of gases, are interesting as emphasizing the analogy between gas pressure and osmotic pressure. If a palladium vessel, heated to 250°–350°, is filled with nitrogen or some other gas not absorbed by palladium, say at atmospheric pressure, and the vessel immersed in hydrogen at a given pressure, the hydrogen will diffuse through the metal membrane till the increase of pressure inside the vessel is nearly equal to the pressure on the outside. For example, in one experiment in which nitrogen was used and the palladium heated to 280°, the two gases being at atmospheric pressure, the excess on the inside was 733 millimeters of mercury and the barometric height was 748.1 millimeters. This may be regarded as the osmotic pressure of nitrogen dissolved in hydrogen.

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[1] THIS JOURNAL, **34**, 1 (1905); **36**, 39 (1906); **37**, 324, 425 and 558 (1907).

[2] Nature, **55**, 253 (1897).

[3] Phil. Trans., **190**, 266 (1897); Nature, **55**, 545 (1897).

[4] Nature, **55**, 272 (1897).

[5] Phil. Mag. [5], **38**, 206 (1894).

The author interprets his results as being in harmony with the view that osmotic pressure is to be ascribed to the dissolved substance, "though apparently caused by entrance of solvent." Whatever interpretation may be given to these observations as bearing on osmotic phenomena of solutions, Lowry[1] directs attention to the fact that here we have a case of a pressure, which is an almost exact analogue of osmotic pressure in liquids, actually produced by the bombardment of the walls of the vessel by nitrogen molecules, and this pressure is independent of the concentration of the hydrogen, inasmuch as the pressure due to hydrogen is the same on the two sides of the septum.

The Surface-Tension Theory.

B. Moore[2] in 1894 put forward the view of surface tension as a possible explanation of osmotic phenomena. Assume two liquids, *A* and *B*, of surface tensions T_1 and T_2, respectively, in vessels connected by a capillary tube of radius r, the liquids meeting in the capillary. Then the skin of liquid forming the surface of contact with the wall of the tube will be urged in the direction of *A*, if T_1 is greater than T_2, by a force $(T_1—T_2)2\pi r$. If the radius of the tube is sufficiently small, that is, small enough to bring all the liquid in it within the range of capillary action, as is probably the case with ordinary osmotic membranes, the whole body of liquid in the capillary will be urged in the direction of *A*. Thus osmosis should proceed in the direction indicated, from the region of less to that of greater surface tension. He states four laws which might be expected to follow: (1) The surface tensions of all solutions obeying the other solution laws should be higher than those of the solvents. (2) For solutions of the same substance in the same solvent, surface tensions should be proportional to the concentration. (3) For solutions of equal concentration of different substances in the same solvent the differences in surface tension between solution and solvent should be the same. (4) In general, for solutions of equal concentration of the same or different substances in different solvents, the difference in surface tension in each case between solution and solvent should be equal. In each of the above laws allowance is to be made, in the case of electrolytes, for the degree of dissociation.

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[1] Trans. Faraday Soc., 3, 12 (1907).

[2] Phil. Mag. [5], 38, 279 (1894).

It is pointed out that solutions of liquids offer the only exceptions to law (1), but that such solutions do not obey the vapor-pressure law either. The work of Quincke[1] and Volkmann[2] on surface tension shows that laws (2) and (4) hold very nearly, while the experimental evidence in regard to law (3) varies.

After a careful comparison of his own results in the surface-tension measurements of a large number of solutions with the osmotic pressures of the same solutions, measured by Overton,[3] Traube[4] states that "among hundreds of combinations.... there is not one in which capillary and osmotic phenomena do not correspond." He arrives at the following conclusions: (1) "The greater the osmotic velocity of a substance soluble in water, the more this substance reduces the capillarity constant of water." (2) "Substances that cannot penetrate membranes (with regard to which the membranes are semipermeable) increase the constant of capillarity of water." (3) "The difference of surface tensions determines the direction and velocity of osmosis," the osmotic flow being always from the region of less to that of greater surface tension. Difference in surface tensions is therefore regarded as "the motive force in osmotic phenomena."

Battelli and Stefanini[5] have called attention to certain cases which do not conform to the rules of Traube. Thus Monte[6] had shown that, although salicin lowers the surface tension of water, when an aqueous solution of this substance and water are separated by a membrane, osmosis takes place in the direction of the solution. Also when ethyl alcohol and water are separated by an animal membrane, the osmotic flow is in the direction of the alcohol, that is, from the region of greater to that of less surface tension. Battelli and Stefanini find the same is true when alcohol and water are separated by a membrane of nickel ferrocyanide. These authors have attempted to reconcile these and other discrepancies by a slight modification of the idea of Traube. They agree with him in ascribing osmotic phenomena to differences in surface tension on the two sides of the membrane, but according to their view, osmosis will proceed in the direction which lends itself best to an equalization of surface tensions. If the membrane is permeable to but one of the liquids, it alone will pass through; if it is permeable to both, osmosis will take place in both directions, till surface tensions are equalized, but at different rates, depending on the specific nature of the two liquids. Thus if the passage of n molecules of water would *increase* the surface tension of the given mass of alcohol less than the passage of n molecules of alcohol would *decrease* the surface tension of the water, then the rate of flow of water will be the *more rapid*. In other words, that liquid of which n molecules will have the *greater* effect on the surface tension of the other will diffuse more *slowly*.

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[1] Pogg. Ann., **160**, 337 and 560 (1877).

[2] Wied. Ann., **17**, 353 (1882); **28**, 135 (1886).

[3] Vierteljahresschr. d. Naturf. Ges. (Zurich), **40**, 159 (1895), and **44**, 88 (1899); Z. physik. Chem , **22**, 189 (1897).

[4] Phil. Mag. [6], **8**, 704 (1904); see also Ann. Phys. u. Chem., **62**, 490 (1897).

[5] Physik. Z., **7**, 190 (1906); J. de Phys., **6**, 402 (1907).

[6] Cim. [4], **5**, 186 (1897).

According to the measurements of Battelli and Stefanini, solutions having equal surface tensions exert the same osmotic pressure regardless of molecular concentration. They found that a 1.78 per cent solution of magnesium sulphate and a 1.11 per cent solution of sodium sulphate have the same surface tension. On placing one of these on the interior and the other on the exterior of an osmotic cell (presumably using a nickel ferrocyanide membrane) no difference of pressure was observed. They experimented in a similar manner with solutions of cane sugar and mannite, copper sulphate and sodium chloride, etc., and always obtained the same result.

The Theories of Poynting and Lowry.

Poynting[1] explains osmotic phenomena on the basis of the formation of labile hydrates, each composed of a molecule of the dissolved substance as a nucleus, surrounded by a number of solvent molecules, the whole forming an unstable complex in which the solvent molecules are constantly changing places. Consider the case of a pure liquid in contact with its vapor. Generally accepted theory postulates a continuous process of evaporation, resulting from molecules striking the surface with sufficient velocity to overcome the attractions of neighboring molecules. This evaporation is balanced by the condensation of practically all the vapor particles impinging on the surface. Now in the case of a solution, the solvent molecules included in the complexes alluded to above are not free to pass out into the region of vapor and hence evaporation proceeds more slowly than from the pure solvent, but these complexes are regarded as quite as effective as solvent molecules in entangling vapor particles coming in contact with the surface separating solution and vapor, which surface is semipermeable as regards solute and solvent. Thus condensation would proceed more rapidly than evaporation till equilibrium between the two is established, both the evaporation and condensation proceeding at a lower rate than in the case of the pure solvent. Essentially the same conditions prevail at the surface of contact of a solution and the more conventional semipermeable membrane, the principal difference being that here we have rigidity and consequently any excess of "condensation" over "evaporation" would give rise to a hydrostatic pressure, which is the measure of osmotic pressure.

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[1] Phil. Mag. [5], 42, 289 (1896).

The theory, when worked out quantitatively and applied to aqueous solutions, leads to the result that substances which are monohydrated should give normal osmotic pressure; substances which unite with two molecules of water should give twice the normal pressure, etc.

Lowry[1] has advanced a conception of osmotic pressure very similar to that of Poynting. Here likewise the retardation of evaporation is brought about by the presence of nonvolatile solute molecules in the surface layer, which may or may not, however, be hydrated, the *modus operandi* being slightly different in the two cases. According to Lowry, if a molecule of solvent strikes one of these solute molecules in the surface layer, it rebounds and is thus prevented from passing into the region of vapor, while condensation proceeds here also as if no solute were present.

The quantitative application of the theory of Lowry follows directly from the relation between osmotic pressure and vapor pressure as worked out by Nernst[2] and, unlike that of Poynting, within certain limits seems to be independent of the complexity of the hydrates formed.

Sutherland's View.

Sutherland[3] offers an explanation of the mechanism of the entrance of solvent into an osmotic cell on the basis of the sievelike action of the membrane. He conceives of the membrane as containing "meshes" large enough to permit the passage of solvent more or less freely while the dissolved molecules are effectually held back. If we assume such a semipermeable membrane separating water and a dilute solution of cane sugar, the sugar molecules, impinging on the "quasi-solid framework" of the membrane, give rise to the pressure just as the impacts of the molecules cause pressure in gases. The laws governing this pressure are the same as in gases, since the phenomena are essentially the same. Consider a membrane with pure water on both sides. The molecules of water in the pores are subject to impacts from other molecules coming from all directions, very much as if no membrane were present. If now we substitute a sugar solution on one side of the membrane, "the sugar molecules are to be regarded as replacing some water molecules, but their collisions on the water in the membrane are rendered inoperative by the shielding action of the framework so that the water molecules in the membrane receive more impacts on the side of the pure water than on the side of the solution and therefore water flows through the membrane" till the excess of hydrostatic pressure on the solution side compensates for the inoperative impacts of the sugar molecules.

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[1] Trans. Faraday Soc., 3, 12 (1907); Phil. Mag. [6], 13, 552 (1907).

[2] Theoretical Chemistry, pp. 124-129.

[3] Phil. Mag. [5], 44, 493 (1897).

A similar mechanical view of Pickering[1] rests on the supposed greater ease with which solvent complexes dissociate, as compared with hydrates in solution. The membrane is supposed to be impermeable to these hydrates and possibly to the larger molecular aggregates in the pure solvent, but permeable to simple water molecules or even to the smaller aggregates.

The "Solution" Theory.

This theory is in substance the following: Given a membrane separating two miscible liquids, A and B, and suppose A to be "soluble" in the membrane or, in other words, that the membrane has the power to absorb A, while B is not soluble. Under these conditions A will dissolve in the membrane on the one side and be given up to B on the other. If the liquid B is in a closed cell, the transfer of A will continue till a definite hydrostatic pressure is developed, the magnitude of which depends on the relative attractions of B and the membrane for A and probably also on the temperature. The action of a copper ferrocyanide membrane separating water from an aqueous solution of cane sugar, for example, depends on the solubility of water and the insolubility of the sugar or the sugar solution, so that the membrane becomes saturated with water with respect to the solvent on the one side, while it is supersaturated with respect to the solution on the other. Hence there is a transfer of solvent across the membrane till the hydrostatic pressure developed becomes sufficient to check the flow.

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[1] Ber. d. chem. Ges., **24**, 3629 (1891).

L'Hermite[1] appears to have been the first to state clearly the view that osmotic phenomena in general are due to this "selective action" of the membrane. According to him endosmose depends on two conditions: (1) The two liquids must be miscible, and (2) one of the liquids at least must be soluble in the membrane. He described a number of "three liquid-layer" experiments which he regarded as typical of osmotic processes in general. For example, he disposed, in a cylinder, layers of ether and chloroform separated by a layer of water and observed that the ether gradually dissolved in the water, to be abstracted, in turn, by the chloroform. By suitable arrangements he was able to show that such transfer resulted in the development of a not inconsiderable pressure.

Kahlenberg[2] in recent years has furnished a considerable amount of evidence in support of this view. He has carried out a large number of experiments on the osmotic pressures of solutions of various kinds, using membranes of rubber and parchment, and has arrived at the following conclusions: (1) Osmosis, both in direction and extent, depends on the specific nature of the membrane used and of the liquids that bathe it; that is, on the "selective action" of the membrane. (2) That the gas laws do not hold for solutions in general. Any agreement between the osmotic pressure of solutions of cane sugar, glucose, etc., and the elastic pressure of gases he would regard as purely fortuitous. (3) Deductions of the thermodynamicist, based on the assumption of a semipermeable membrane, are valueless and misleading, since a perfectly semipermeable membrane is experimentally impossible.

Armstrong's Theory.

Prof. Armstrong[3] explains osmotic and related phenomena on an association, rather than a dissociation, hypothesis. All liquids are regarded as in some degree associated. In water, for example, we have probably both simple and polymerized molecules, in equilibrium, represented thus: $(H_2O)_n \rightleftarrows nH_2O$. The addition of a nonelectrolyte involves a disturbance of equilibrium in the direction $(H_2O)_n \rightarrow nH_2O$. These monads are regarded as exerting an attraction for similar molecules in the region of pure solvent or of a more dilute solution. There will accordingly be a transfer of solvent across the membrane till equilibrium is reëstablished, the osmotic attraction, in the case of a nonelectrolyte, being due wholly to the influence of the dissociated water complexes.

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[1] Ann. Chim. Phys. [3], **43**, 420 (1855); Compt. rend., **39**, 1177 (1854).

[2] J. Physic. Chem., **10**, 141 (1906). See also Trans. Faraday Soc., **3**, 23 (1907) and various articles in Nature.

[3] P. Roy. Soc. [A], **78**, 264 (1906).

Electrolytes, besides producing this dissociation effect, are supposed also to exert an additional attractive influence on the solvent molecules and therefore show a greater osmotic pressure than equivalent molecular concentrations of nonelectrolytes.

In concluding this review, it may be said that those who hold to the thermodynamic explanation of osmotic phenomena do not regard it as necessarily excluding the views which are concerned primarily with the mechanism by which the solvent enters the cell, such as the "solution theory," advocated by Kahlenberg. Findlay[1] states that "in thermodynamics, they did not consider at all how the membrane acts, provided the changes in energy were equal in opposite directions." Whetham[2] says that "it is the strength of thermodynamic reasoning that it avoids the uncertainties of definite hypotheses about the mechanism of the connection between the two series of phenomena it correlates; it is the weakness of thermodynamic reasoning that it fails to throw light on the ultimate structure of the system which such hypotheses seek to examine." And hence, although van't Hoff, in his original paper, attributed osmotic pressure to the bombardment of the membrane by the molecules of the dissolved substance, the validity of his deductions is not dependent upon the correctness of this hypothesis. As Whetham remarks,[3] the pressure "may be due to molecular impacts, or to chemical affinity, or to some other undiscovered cause."

B. F. LOVELACE.

JOHNS HOPKINS UNIVERSITY,
March 2, 1908.

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[1] Trans. Faraday Soc., **3**, 30 (1907).

[2] *Ibid.*, **3**, 34 (1907).

[3] Nature, **74**, 54 (1906).

THE DEGRADATION OF THE ELEMENTS.

A short paper[1] of unusual significance, bearing the above title, has recently been published by Sir William Ramsay. In this communication there is discussed all that is known in reference to the production of one elementary form of matter from another.

Ramsay starts out with the proposition that[2] "every scientific discovery is a function of two conditions—the concentration of a certain quantity of energy in a small volume, and the possibility of directing this energy to a given end."

He points out that the greatest concentration of energy with which we are familiar is in the radium emanation. A given volume of the emanation will give out *two and a half million times as much heat* as would be set free by the union of hydrogen and oxygen in an equal volume of detonating gas, and this is one of the most exothermic of chemical reactions. It is thus obvious that there is no comparison between the amount of intrinsic energy contained in the radium emanation and that present in the most active chemical elements—the ratio being as millions to one.

The radium emanation is a gas, having a molecular weight of probably about 200. It is unstable, undergoing decomposition spontaneously, yielding the element helium. Like argon, helium, neon, etc., it resists the action of all chemical reagents and is placed by Ramsay with the noble gases:

Noble gases	He	Ne	Ar	Kr	Xe	Emanation
Atomic weights	4	20	39.9	81.8	128	200—216.5

The most interesting and suggestive part of Ramsay's paper may be reviewed as follows: The emanation, as we have seen, undergoes decomposition spontaneously, giving among other things the element helium. If the emanation is allowed to stand in the presence of water, the water is decomposed into its elements, but not in the ratio in which they occur in water. There is always an excess of hydrogen—about 5.5 per cent on an average, the excess of hydrogen varying in a series of nine determinations from 3.65 to 16 per cent.

Under these conditions the emanation produces only traces of helium, *neon* being formed in appreciable quantity. Ramsay interprets these facts in the following manner: Much of the energy in the emanation is expended in doing the work necessary to decompose water, and the emanation itself is not "degraded" to its lowest term, helium, but the degradation stops at the second member, neon, with an atomic weight of 20.

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[1] J. Chim. Phys., **5**, 647 (1907).

[2] *Loc. cit.*, p. 647.

Finally, allow the emanation to act on a salt of copper. According to Ramsay there is formed not only sodium, but a trace of lithium. The gas produced is not helium, not neon, but *argon.*

The interpretation here is analogous to that given above, where the emanation is allowed to decompose water. The intrinsic energy of the emanation is expended to a greater extent in doing the larger amount of work required to "degrade" the copper, and, consequently, a smaller amount remains to degrade the emanation itself. The result is that the emanation, under these conditions, does not yield helium, does not yield neon, but argon which has a larger atomic mass.

Ramsay concludes by stating that in the gas which is given off spontaneously from a solution of thorium nitrate, he finds carbon dioxide. He points out that carbon is the first member of the natural family of which thorium has the largest atomic weight.

He raises the question as to whether the carbon may not be produced as the result of the degradation of the thorium by the intrinsic energy in the latter, which, as we know, is also radioactive. H. C. J.

REVIEWS.

COMMERCIAL ORGANIC ANALYSIS. A Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicines, Etc. By ALFRED H. ALLEN. Volume II., Part 3, Third Edition. Rewritten and revised by the Author and ARNOLD RAMSBY TANKARD. Philadelphia: P. Blakiston's Sons & Co. 1907. pp. xii + 547. Price, $5.

The appearance of this new edition of Part 3 completes the third edition of Volume II. of this helpful and extensive treatise on Commercial Organic Analysis. The first portion of the volume is devoted to the aromatic acids, the subject matter being greatly amplified as compared with the second edition. But the distinctive mark of the volume is the thorough discussion of resins and essential oils, in keeping with the great advances made in this field during recent years. The four hundred pages given to these last subjects are a striking contrast to the scant twenty-five pages of the first edition. It is a matter for congratulation that this mass of material, widely scattered through chemical literature, has been assembled in concise and attractive form. And it is not a mere compilation of analytical methods, for each subject is headed by a brief theoretical discussion which makes the volume instructive reading. Frequent tables, summarizing the properties of related compounds, add to its convenience as a laboratory reference book. References to the literature are to be found on practically every page, but it is to be regretted that this feature has not been made complete.

Where there is so much to be commended, it seems scarcely just to criticize minor errors, and yet there are a number of these which indicate carelessness. To one not familiar with the literature of the subject, the incorrect "Mauch" on pages 146 and 148, with no reference given, is apt to be confusing in view of the correct spelling "Mach" on pages 159 and 160. The expression (page 165) "is boiled with 50 cc. of alcoholic potash" leaves no room for doubt as to volume, but it is indefinite as to concentration. The description (page 142) of Tschirch's method for the proximate analysis of resinous substances is erroneous in that Tschirch, after separation of the resin acids, removes the ether, *then* subjects the residue to steam distillation. The opinion of the authors (page 146) that two carboxyl groups appear to exist in the molecule of abietic acid is flatly contradicted on page 160 by the sentence "Abietic acid is frequently described as dibasic but the presence of only one carboxyl group in the molecule and the proportion of alkali required for its neutralization conclusively negatives this view." On page 161, the unsaponifiable portion of colophony (resene) is stated probably to "consist chiefly of hydrocarbons of the nature of resin oil, produced by the action of heat on the colophony during the process of manufacture." In this view, the authors are evidently following Fahrion. But this probability rapidly changes to improbability if we accept the work of Tschirch, who finds an even higher percentage of this unsaponifiable matter (resene) in the oleo-resin from which colophony is manufactured. In the footnote on page 157 the assertion is made that "the resin from a given tree also becomes darker year after year." Abundant demonstration has been made that this increasing coloration of the resin is due solely to the method of collecting the crude turpentine from which the resin is obtained. Collected under similar conditions in succeeding years of operation, no change in the color of the resin can be detected. The first paragraph of the section on "Common Turpentine," page 196, is so filled with errors that it should be entirely rewritten.

These criticisms, however, are on minor points and do not affect the great value of the work as a most helpful laboratory guide in a difficult subject.

CHAS. H. HERTY.

MERCK'S 1907 INDEX (Third Edition). An Encyclopedia for the Chemist, Pharmacist, and Physician, Stating the Names and Synonyms; Source or Origin; Chemical Nature and Formulas; Physical Form, Appearance and Properties, Melting and Boiling Points; Solubilities; Specific Gravities and Methods of Testing; Physical Effects; Therapeutic Uses; Modes of Administration and Application; Ordinary and Maximum Doses; Incompatibles; Antidotes; Special Cautions; Hints on Keeping and Handling, Etc., of the Chemicals and Drugs used in Chemistry, Medicine and the Arts. New York, St. Louis, Mo., Rahway, N. J.: Merck & Co.

The title page shows clearly what this publication is intended for. It will be found very useful as a book of reference, especially in these days when the chemist finds it extremely difficult to keep abreast of the times in the flood of new remedies with meaningless names. It contains a vast amount of valuable information so presented that anything wanted can readily be found.

UEBUNGSBEISPIELE AUS DER ANORGANISCHEN EXPERIMENTALCHEMIE. Von HEINRICH BILTZ und WILHELM BILTZ. Mit 26 Textfiguren. Leipzig: Wilhelm Engelmann. 1907. pp. 232. Price, 7 M.

At first sight this book would be considered simply a manual of inorganic preparations, containing many familiar preparations, and many not usually included in such manuals, among which may be noted elements obtained by Goldschmidt's method of reduction by aluminium, colloidal elements, salts of complex acids, and a number of metal-ammonium salts. The book closes with a chapter on the preparation of compounds of the rare earths from minerals.

A closer examination shows many experiments designed to illustrate physical-chemical laws and methods, and a series of well written introductions to the several sections of the book, in which the writers discuss recent theories and methods. For example, in the chapter on the salts of halogeno-acids (such as silicofluorides) and on complex cyanogen compounds (such as potassium cobalticyanide) the authors refer to the work of Abegg, to Bodländer's measurements of the stability constants of the complex anions containing metal, and to Werner's theory of primary and secondary valence (Neben-Valenzen) to explain the structure of this type of compounds.

From what has been said it is evident that this is not a book for beginners, indeed the writers say so in their preface. It would be a most valuable book for American post-graduate students, and teachers of inorganic chemistry will find it interesting and useful to select work for their students, as most of the preparations are not too difficult for an undergraduate student who has had some practice in preparation work.

E. R.

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CHEMICAL JOURNAL

[Contributions from the Sheffield Laboratory of Yale University.]

CLV.—THE POLYIODIDES OF POTASSIUM, RUBIDIUM AND CAESIUM.

By H. W. Foote and W. C. Chalker.

The polyiodides of the alkalis have recently been investigated by Abegg and Hamburger,[1] who have attempted to determine all those that form stable solids at 25°. The method used by these investigators consisted essentially in treating an alkali iodide with varying amounts of benzene which was nearly saturated with iodine and shaking the mixtures in a thermostat till there was no further change in the concentration of iodine in the benzene. By this process iodine was withdrawn from solution by the alkali iodide, which was partially converted into a periodide. The concentration of iodine in the benzene solution when equilibrium was reached was constant as long as the two iodides were present as solids. The concentration changed to a new and constant value when the amount of iodine present was sufficient to convert all the iodide into a mixture of periodides. By taking into account the amount of the constituents used and noting when the changes in concentration occurred, the authors drew conclusions in regard to the composition of the polyiodides which were formed. They concluded that the following periodides exist as solids at 25°:

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[1] Z. anorg. Chem., 50, 403, 1906.

KI_7; NH_4I_3; RbI_3, RbI_7, RbI_9; CsI_3, CsI_5 or CsI_7, CsI_9.

The method which was used is undoubtedly correct in principle and might lead to correct conclusions, but the compounds differ widely from those obtained before by other investigators.

Johnson[1] has described the compound KI_3, which was not found by Abegg and Hamburger. He analyzed it repeatedly and determined its specific gravity. The same compound has also been obtained by Wells and Wheeler[2] and its crystallography determined. The periodides of rubidium and caesium have been investigated by Wells and by Wells and Wheeler,[3] who obtained the compounds RbI_3, CsI_3 and CsI_5. These authors state that attempts to prepare an iodide higher than KI_3 or RbI_3 were unsuccessful. The solubility relations of the periodides of caesium have been studied by Foote,[4] but this work seems to have been overlooked by Abegg and Hamburger. The solubility in water of varying mixtures of caesium iodide and iodine was determined at temperatures both above and below 25°, the temperature at which Abegg and Hamburger worked. The method was in principle not unlike that used later by Abegg and Hamburger but it had the advantage that both caesium iodide and iodine dissolved in water and could be determined, while in benzene only iodine was determined. Just as in the benzene solution, constant concentration of iodine indicated a mixture of two iodides, so here a constant concentration of caesium iodide and iodine indicated a mixture. When the composition of the solution changed to a new constant value it indicated a change in the solid phases present, precisely as was the case with the benzene solution. Knowing the amounts of the constituents present, it was an easy matter to determine what solid phases were present. The following table, taken from the article referred to, gives the results obtained:

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[1] J. Chem. Soc., **1877**, 249.

[2] Z. anorg. Chem., **1**, 442.

[3] *Ibid.*, **1**, 85, 442; **2**, 255.

[4] THIS JOURNAL, **29**, 203 (1903).

Table I.—Solubility of Caesium Iodides.

Temperature.	(1) Pure CsI.	(2) CsI and CsI_3.		(3) CsI_3 and CsI_5.		(4) CsI_5 and I.	
	CsI. Per cent.	CsI. Per c't.	I. Per c't.	CsI. Per c't.	I. Per c't.	CsI. Per c't.	I. Per c't.
Cryohydric	27.73	27.53	0.09	3.14	0.25	0.88	0.35
	27.64	27.51	0.09	3.59	0.35	0.84	0.34
	T = —4°.0	T = —4°.0		2.82	0.35	0.83	0.34
				T = —0°.4		T = —0°.2	
35°.6	51.35	51.49	0.71	10.67	1.75	3.66	1.47
	51.61	51.84	0.71	10.78	1.86	3.82	1.73
52°.2	...	...	....	16.51	4.34	6.45	3.52
				17.06	4.70	6.99	3.13
						6.87	3.29
						6.44	3.61

In the table, it will be noticed that the composition of the solutions under (2), (3) and (4) was constant at a given temperature, although the residues which gave constant results were purposely varied greatly. From the results it was concluded that CsI_3 and CsI_5 are formed at all the temperatures investigated and that no other periodides are formed.

The objection that may be raised to the results given in the table is that the composition of the residues is not given—an objection that holds to a great extent in the results of Abegg and Hamburger—so that, for instance, the results under (4) would not show that CsI_9 did not exist since it was not shown that the residues in the experiments contained percentages of iodine both greater and less than the percentage of iodine in CsI_9. While the composition of the residues was varied greatly, we do not now know their exact composition and it seemed advisable to carry out a few experiments at 25° by the same method used before and, in addition, to determine accurately the composition of the residues. We have also carried out similar experiments with potassium and rubidium iodides.

In every case weighed amounts of the iodide and iodine were treated with a known quantity of water in small glass-stoppered bottles. The heads of the bottles were dipped in melted paraffine to make them perfectly tight. The bottles were usually warmed for some time in a beaker of water, with thorough shaking, and then placed in a thermostat kept at 25° and shaken for a number of days. We had no difficulty, under these conditions, in obtaining saturated solutions. The liquid was removed for analysis by drawing it into a pipette through a plug of glass wool. The liquid was weighed in two portions. One portion was used to determine available iodine by titration with thiosulphate. Alkali iodide was determined in the other by evaporating to dryness and igniting gently. The residues were freed from the mother liquors as rapidly and thoroughly as possible by pressing between filter paper. Alkali iodide was determined in them by ignition.

Caesium Polyiodides.

Most of the caesium iodide-iodine mixtures were prepared by using calculated amounts of caesium triiodide in place of caesium iodide, as we had a supply of exceedingly pure triiodide on hand. One or two mixtures, however, were prepared by using caesium iodide obtained by igniting the triiodide. It was an easy matter to prepare mixtures in which the residues, after shaking, would have approximately any composition desired, since the composition of the solutions at 25° could be approximately calculated in advance by interpolation from the results in Table I.

As there appears to be no question that CsI_3 forms and that no periodide lower than this exists, only those mixtures were prepared whose residues would contain more than 49.42 per cent available iodine, which is the amount in caesium triiodide. The following results were obtained:

Table II.—Solubility of Caesium Iodides at 25°.

	Solution.		Residue. Per cent available I.	Empirical composition of residue.	Residue contains:
	Per cent CsI.	Per cent I.			
1	7.72	1.18	52.86	$CsI_{3.29}$	CsI_3 and CsI_5
2	7.69	1.19	59.32	$CsI_{3.98}$	
3	2.40	1.23	69.88	$CsI_{5.75}$	CsI_5 and Iodine
4	2.35	1.23	75.84	$CsI_{7.43}$	
5	2.39	1.25	89.93	$CsI_{19.3}$	

The results are very sharp and confirm the results obtained by Wells and Wheeler and our own previous conclusions that only CsI_3 and CsI_5 exist as solids at 25°. They show constant solubility while the composition of the residue lies between that of CsI_3 and CsI_5 and they show a second constant solubility for all mixtures higher in iodine than corresponds to CsI_5, proving that CsI_7 and CsI_9 do not form. If CsI_9, for instance, had formed, the solubility in No. 4 would have been different from that in No. 5, since different phases would have been present.

Potassium Polyiodides.

The periodides of potassium are extraordinarily soluble in water, but when this was taken into account it was not a difficult matter to prepare mixtures which gave residues, after shaking, varying from nearly pure potassium iodide to nearly pure iodine. The results obtained when mixtures of two iodides were present in the residues are given in Table III.

Table III.—Solubility of Potassium Iodides at 25°.

	Solution.					
	(1) Per cent KI.	(2) Per cent I.	(3) Per cent I minus per cent KI.	Residue. Per cent KI.	Empirical composition.	Residue contains:
1	29.45	64.34	34.89	94.10	$KI_{18.2}$	KI and KI_3
2	28.91	63.88	34.97	44.28	$KI_{2.65}$	
3	26.84	66.54	39.70	29.81	$KI_{4.08}$	KI_3 and KI_7
4	27.18	67.14	39.96	27.73	$KI_{4.41}$	
5	27.14	66.60	39.46	19.29	$KI_{6.48}$	
6	25.88	68.79	42.91	16.16	$KI_{7.79}$	KI_7 and Iodine
7	25.57	69.01	43.44	11.96	$KI_{10.6}$	

The change in concentration from one constant value to the next, when the solid phases change, is slight. It can perhaps be shown best by the difference between the concentration of iodine and potassium iodide, which is given in column (3). It will be seen that the solubility remains constant in each group. It changes when the residues change from the empirical composition $KI_{2.65}$ to $KI_{4.08}$, showing that

KI_3 undoubtedly exists. This confirms the work of Johnson and of Wells and Wheeler but does not agree with the results obtained by Abegg and Hamburger. The solubility changes again when the residue changes from $KI_{6.48}$ to $KI_{7.79}$, showing the formation of KI_7. This is the only one of the five new compounds described by Abegg and Hamburger whose existence we have been able to confirm.

Mixtures were also prepared in which the constituents were present in such proportions that the pure compounds would be formed. It is evident that pure potassium triiodide can exist in contact with solutions varying from the composition of Nos. 1 and 2 to that of Nos. 3 to 5 (Table III.), and the heptaiodide with solutions varying from the composition of Nos. 3 to 5 to that of Nos. 6 and 7. The following results (Table IV.) give the composition of solutions and residues when the pure compounds were present:

Table IV.—Solubility of Potassium Iodides at 25° (Continued).

	Solution.		Residue.	Residue contains:
	Per cent KI.	Per cent I.	Per cent KI.	
1	27.86	66.56	40.54	KI_3
2	27.27	66.91	40.11	Calculated per cent KI = 39.55
3	26.95	67.17	18.52	KI_7
4	25.71	67.91	18.60	Calculated per cent KI = 17.96

We consider the results in Tables III. and IV. sufficient to show that the compounds KI_3 and KI_7 are the only periodides which form solids at 25°.

Rubidium Periodides.

To prepare rubidium iodide, we used rubidium chloride which had previously been very carefully purified in this laboratory. It was converted into the nitrate and then into the carbonate by strong ignition with an excess of pure oxalic acid. This was dissolved in hydriodic acid and evaporated to dryness.

The entire series of results obtained is given below (Table V.):

Table V.—Solubility of Rubidium Iodides at 25°.

	Solution.		Residue.	Empirical	Residue
	Per cent RbI.	Per cent I.	Per cent RbI.	composition.	contains:
0	61.93	0	100	RbI	RbI
1	59.99	5.87	93.75	$RbI_{1.11}$	RbI
2	59.88	5.93	58.34	$RbI_{2.20}$	RbI_3
3	57.24	8.02	46.33	$RbI_{2.94}$	RbI_3
4	33.89	38.08	45.42	$RbI_{3.01}$	
5	28.01	64.85	37.95	$RbI_{2.74}$	RbI_3 and Iodine
6	27.85	65.12	29.70	$RbI_{4.96}$	
7	27.83	65.13	23.57	$RbI_{5.43}$	
8	27.99	64.98	14.09	$RbI_{11.2}$	

From the results it will be seen that the solubility is constant in Nos. 1 and 2, where a mixture of RbI and RbI_3 is present, and it is constant again in Nos. 5 to 8, where the residues vary from the empirical composition $RbI_{3.74}$ to $RbI_{11.2}$. The latter results show that RbI_7 and RbI_9 did not form, which agrees with the observations of Wells and Wheeler.

Summary.

1. Abegg and Hamburger state that the following alkali periodides form at 25°: KI_7, RbI_3, RbI_7, RbI_9, CsI_3, CsI_5 or CsI_7, CsI_9.

2. Previous investigators have found the following compounds: KI_3, RbI_3, CsI_3, CsI_5.

3. We have found at 25° the compounds KI_3, RbI_3, CsI_3, CsI_5 described by previous investigators, and also KI_7, described by Abegg and Hamburger. We find no indication whatever of the existence of the compounds RbI_7, RbI_9, CsI_7 and CsI_9, mentioned by Abegg and Hamburger.

[Contributions from the Chemical Laboratory of Harvard College.]

MERCURY SALTS OF THE THREE NITRANILINES.

By C. Loring Jackson and R. W. Peakes.

The abnormal replacement of bromine by hydrogen in 1,3,5-tribrom-2,4-dinitrobenzene and allied compounds has been studied for some years in this laboratory. In the hope of finding new cases of this sort, we undertook the investigation of the behavior of this substance with the 3 nitranilines, and when, as was not entirely unexpected, the two substances did not react under any conditions we could find, we prepared the mercury salts, which might well give a better result.

On boiling a nitraniline with water and freshly prepared mercuric oxide, a red salt was formed, which, however, under these conditions, we could not obtain free from mercuric oxide, even when a large excess of the nitraniline was used; but, when the mercuric oxide acted in the nascent state, the substances were obtained pure with little trouble. The process consisted in mixing aqueous solutions of the nitraniline and mercuric nitrate and adding to the mixture potassic hydrate, when, after standing, the salt came down as a red precipitate, which was purified by washing with water and ether.

The para and ortho salts have the formula $(C_6H_4NO_2NH)_2Hg$; the meta salt seems to be $(C_6H_4NO_2NH)_2Hg.H_2O$. This theory derived from the analyses is supported by the fact that it has a much deeper color than the other two salts, being maroon while the para salt is vivid crimson and the ortho bright red. If this darker color is due to a molecule of water of crystallization, it is probable that the para salt also was occasionally deposited with water of crystallization, since now and then it appeared of a purplish-crimson color, which turned to bright crimson, with no trace of purple, on drying *in vacuo*. Of the three salts, the ortho was formed most rapidly, the meta next, and the para most slowly. The salts proved much less reactive than had been hoped, as they gave no better results with the tribromdinitrobenzene than the free nitranilines, although, on the other hand, they were decomposed by iodine in benzene solution, and hydrochloric acid dissolved them at once.

So far as we can find, these salts are new, but Pesci,[1] by the same process, had obtained the aniline salt, $(C_6H_5NH)_2Hg$, some years previously. Although our salts undoubtedly correspond to Pesci's, there are marked differences between the two sets in physical properties, since the aniline salt is colorless and somewhat soluble in water, while the nitraniline salts are intensely colored in various shades of red and essentially insoluble.

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[1] Gazz. chim. ital., 28 [2], 443.

EXPERIMENTAL.

Preparation of the Mercury Salts of the Three Nitranilines.—A saturated solution of the nitraniline in water at ordinary temperatures was made, and to one liter of this was added slowly, with constant stirring, an aqueous solution of mercuric nitrate containing enough nitric acid to hold the salt in solution. The reagents were mixed in the proportion of a little more than one molecule of the nitrate to two of the nitraniline, the amount of the latter being calculated from its solubility in water, which gave a sufficiently accurate result for this purpose. A strong solution of potassic hydrate was then added slowly and with constant stirring until the alkali was present in excess, when the mixture was allowed to stand for some time with occasional stirring. On the addition of the potassic hydrate there was at first a slight milky precipitation, which was soon replaced by the dark-red mercury salt. With ortho- or metanitraniline the standing, after the addition of the alkali, should last over an hour; with the para compound, much longer. In working with the metanitraniline we were sometimes embarrassed by the formation of a brown, inorganic precipitate, which we recognized as the oxychloride of mercury, formed from an impurity of chloride in the potassic hydrate used. Its formation was usually avoided by adding the alkali more rapidly than in the case of the para or ortho body. After the precipitate of the organic salt had formed and settled, the supernatant liquid was decanted and the solid washed on a filter several times with water, which removed the inorganic impurities and part, but not all, of the nitraniline. The precipitate was then dried and washed with ether until the washings became colorless, when it was dried *in vacuo* for analysis.

The same salts, to judge from their color, were formed on boiling the nitranilines with freshly precipitated mercuric oxide and water, but we did not succeed in converting all the mercuric oxide into the salt, even when a large excess of nitraniline was used, and therefore abandoned this method of preparation. Mercuric nitrate gave no precipitate with a cold solution of a nitraniline but formed one, to a limited extent, with a hot, saturated solution; as this precipitate seemed to be a mixture of several substances, we did not undertake its study.

Paranitraniline Salt, $(C_6H_4NO_2NH)_2Hg$.—All the salts were analyzed by dissolving in water and hydrochloric acid and precipitating with sulphuretted hydrogen the mercuric sulphide, which was weighed on a Gooch crucible. Washing the mercuric sulphide with carbonic disulphide, in one or two cases, produced no change in weight.

I. 0.3588 gram substance gave 0.1727 gram HgS.
II. 0.6622 gram substance gave 0.3175 gram HgS.
III. 0.1346 gram substance gave 0.0647 gram HgS.

	Calculated for $(C_6H_4NO_2NH)_2Hg$.	Found. (I.)	(II.)	(III.)
Hg	42.19	41.50	41.33	41.45

Properties of the Paranitraniline Salt.—This salt is precipitated sometimes as a purplish-crimson powder, which becomes brilliant crimson on drying; in other preparations the precipitate is brilliant crimson from the first. It seems to be slightly soluble in pyridine but insoluble in water, alcohol, ether, acetone, chloroform, ethyl acetate or benzene. It is slowly decomposed by standing with alcohol. Hydrochloric acid decomposes and dissolves it.

Metanitraniline Salt, $(C_6H_4NO_2NH)_2Hg.H_2O$.

I. 0.1188 gram substance gave 0.0559 gram HgS.
II. 0.4584 gram substance gave 0.2128 gram HgS.
III. 0.4743 gram substance gave 0.2205 gram HgS.

	Calculated for $(C_6H_4NO_2NH)_2Hg$.	Found. (I.)	(II.)	(III.)
Hg	42.19	40.57	40.00	40.08

These analyses show that the substance is not the simple salt, as was the case with the paranitraniline. If it contains one molecule of water of crystallization, the percentage of mercury is as follows:

	$(C_6H_4NO_2NH)_2Hg.H_2O$.
Hg	40.64

This value agrees sufficiently well with those found. The theory that the meta compound contains water of crystallization receives a certain confirmation from the fact that it has a much darker color than either the para or the ortho salt, and it can be accepted with safety, we think, until it has been tested by experiment.

Properties of the Metanitraniline Salt.—It forms a maroon-colored powder when dried *in vacuo*. The precipitate is less bulky and forms more slowly than that from the orthonitraniline, but forms more quickly and is more bulky than the para salt. It is insoluble in water or the common organic solvents.

Orthonitraniline Salt, $(C_6H_4NO_2NH)_2Hg$.

I. 1.2282 grams substance gave 0.6001 gram HgS.
II. 0.5346 gram substance gave 0.2550 gram HgS.
III. 0.4786 gram substance gave 0.2288 gram HgS.

	Calculated for $(C_6H_4NO_2NH)_2Hg$.	Found. (I.)	(II.)	(III.)
Hg	42.19	42.12	41.11	41.20

The necessity for washing with ether was shown by the analysis of a specimen washed only with water, which gave 40.89 per cent of mercury.

Properties of the Orthonitraniline Salt.—A bright-red powder, which forms more quickly and appears as a more bulky precipitate than the two isomeric salts. Insoluble in water and the common organic solvents.

After we had determined that 1,3,5-tribrom-2,4-dinitrobenzene did not react on the nitranilines either in solution in water, alcohol, or alcohol and benzene, or when the two substances were fused together, we tried the action of the same tribromdinitrobenzene on our mercury salts, both in presence of benzene and of benzene and alcohol, but even after 9 hours' boiling there were no signs of a reaction. Iodine, on the other hand, in benzene solution, acted upon the mercury salts, but the work was undertaken too late in the year for us to study the product.

Attempts to Make Other Nitraniline Salts.—Solutions of orthonitraniline in water were added, in one experiment, to a solution of cupric sulphate, in another to a solution of plumbic acetate; on adding potassic hydrate the metallic hydrate was obtained in each case with no admixture of an organic salt.

In the hope that the hydrogen attached to the nitrogen might be replaced by sodium if it were rendered more reactive, the benzoylnitranilide was made by allowing the solid nitraniline to stand with benzoyl chloride overnight (so far as we can find it has not been made in this way before); and this compound, dissolved in absolute alcohol, was allowed to stand with sodic ethylate, but, although the solution turned yellow, on addition of ether no precipitate was obtained. It seems probable, therefore, that no salt was formed, which is strange when it is remembered that acetanilide gives a sodium salt.

CAMBRIDGE, MASS.,
August 29, 1907.

DIETHYLISOPROPYLMETHANE.

BY LATHAM CLARKE.

This paper describes the synthesis of diethylisopropylmethane, which forms part of a research on the octanes, undertaken some time ago in this laboratory.[1]

The hydrocarbon was made by two different methods, and in this way its constitution was confirmed.

In the preparation of diethylisopropylmethane, the simplest procedure is as follows: From ethyl acetacetate is made ethyl diethylacetacetate which, on saponification, gives 3-ethyl-2-pentanone or diethylacetone, $CH_3COCH(C_2H_5)_2$. This is subjected to the Grignard reaction, using magnesium and methyl iodide, and a carbinol is produced, having the structure

$$(CH_3)_2C(OH)CH(C_2H_5)_2,$$

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[1] Preliminary notice, Ber. d. chem. Ges., 40, 352.

which, when converted into the corresponding carbinol iodide and reduced, yields the desired octane.

To summarize these reactions:

$$CH_3COCH_2CO_2C_2H_5 \rightarrow CH_3COC(C_2H_5)_2CO_2C_2H_5 \rightarrow$$
$$CH_3COCH(C_2H_5)_2 \rightarrow (CH_3)_2C(OH)CH(C_2H_5)_2 \rightarrow$$
$$(CH_3)_2C(I)CH(C_2H_5)_2 \rightarrow (CH_3)_2CHCH(C_2H_5)_2.$$

The second method consists in making ethyl ethylisopropylacetacetate and saponifying it, with the formation of 3-isopropyl-2-pentanone, or ethylisopropylacetone,

$$CH_3COCH(C_2H_5)(CH(CH_3)_2).$$

By reducing this to the carbinol, converting the carbinol into the corresponding carbinol iodide, and reducing, the octane diethylisopropylmethane is obtained. These reactions may be summarized as follows:

$$CH_3COCH_2CO_2C_2H_5 \rightarrow CH_3COC(C_2H_5)(CH(CH_3)_2)CO_2C_2H_5 \rightarrow$$
$$CH_3COCH(C_2H_5)(CH(CH_3)_2) \rightarrow$$
$$CH_3CHOHCH(C_2H_5)(CH(CH_3)_2) \rightarrow$$
$$CH_3CH(I)CH(C_2H_5)(CH(CH_3)_2) \rightarrow$$
$$CH_3CH_2CH(C_2H_5)(CH(CH_3)_2).$$

Both methods yielded identical products.

The first method is, however, the better one, as the reactions proceed more smoothly and the yield is better. In the second method, in the saponification of ethyl ethylisopropylacetacetate by caustic potash, the reaction takes place very slowly, the yield of the ketone, 3-isopropyl-2-pentanone,

$$CH_3COCH(C_2H_5)(CH(CH_3)_2),$$

being only about 25 to 30 per cent of the theoretical after a week's treatment. The great stability toward alkalis manifested by the ester,

$$CH_3COC(C_2H_5)(CH(CH_3)_2)CO_2C_2H_5,$$

is accounted for by the spatial configuration. The ethyl and the large isopropyl group, both of which are on the same carbon atom, shield the carboxyl from the splitting action of the alkali. It is interesting to note that the corresponding diethyl derivative of ethyl acetacetate,

$$CH_3COC(C_2H_5)_2CO_2C_2H_5,$$

is decomposed almost completely under the same conditions by 8 hours' boiling.

EXPERIMENTAL.

First Method.

Ethyl diethylacetacetate, $CH_3COC(C_2H_5)_2CO_2C_2H_5$, was prepared by Conrad's method,[1] and saponified by boiling for 8 hours with a 10 per cent solution of caustic potash. The resulting ketone was distilled with steam, separated, dried with calcium chloride, and fractionated several times with great care with a Hempel column until a fraction boiling sharply at 138° at 760 mm. pressure was obtained. Ethyl diethylacetacetate usually gave a yield of 60 per cent of 3-ethyl-2-pentanone of this degree of purity.

3-Ethyl-2-methyl-2-pentanol, $(CH_3)_2C(OH)CH(C_2H_5)_2$.—3-Ethyl-2-pentanone, a ketone containing seven carbon atoms, was converted into 3-ethyl-2-methyl-2-pentanol, a carbinol with eight carbon atoms, by the Grignard reaction.

Twenty-four grams of magnesium turnings were dissolved in a mixture of 160 grams of methyl iodide and 100 grams of dry ether. To this, the ketone (100 grams), which was mixed with an equal volume of ether, was slowly added and the mixture set aside overnight. Next day ice and water were added until the magnesium-organic body was decomposed, and the mixture was then neutralized with hydrochloric acid: the ether layer was separated, the ether distilled off, and the residue dried over 50 per cent caustic potash solution. On fractionation, this yielded 18 grams of a liquid boiling at 156° at 760 mm. pressure. This liquid was 3-ethyl-2-methyl-2-pentanol. The residue from the carbinol contained other higher boiling liquids which have not yet been investigated but which will be studied in the future.

On analysis, 3-ethyl-2-methyl-2-pentanol gave the following results:

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[1] **Conrad and Limpach: Ann. Chem. (Liebig), 192, 153.**

0.2478 gram substance gave 0.6694 gram CO_2 and 0.31 gram H_2O.

	Calculated for $C_8H_{18}O$.	Found.
C	73.85	73.69
H	13.85	13.90

Properties.—Liquid; boils at 156° under 760 mm. pressure; has a rather strong aromatic odor; and is miscible with ether, methyl alcohol, ethyl alcohol, benzene, toluene, ligroin and chloroform.

3-Ethyl-2-methyl-2-iodopropane, $(CH_3)_2C(I)CH(C_2H_5)_2$, *and its Reduction to Diethylisopropylmethane.*—For the preparation of 3-ethyl-2-methyl-2-iodopropane, 26 grams of 3-ethyl-2-methyl-2-pentanol were mixed with 2.6 grams of red phosphorus and 26 grams of iodine, and allowed to stand one hour at room temperature, after which the mixture was heated on the water bath at 60° for ten hours. The resulting iodide was decanted from the unchanged phosphorus and washed with water, but was not distilled.

It was reduced to the hydrocarbon without further purification by the following method: A 500 cc. round-bottom flask, fitted with a return condenser, was half filled with granulated zinc, the iodide was poured in, and concentrated (40 per cent) hydrochloric acid was added in small portions. The whole was heated to about 70°. At first, the heavy iodide rested on the bottom of the flask, but as the reduction proceeded the octane collected on the upper surface of the acid. This floating layer, however, still contained much unchanged iodide, which was removed by the nascent hydrogen set free at the plane of contact between the two liquid layers, the amount of zinc present being purposely kept large enough to admit of this. The action was allowed to go on about two hours, at the end of which time the octane was separated, dried over calcic chloride, then twice distilled, and a fraction boiling at 110° to 120° collected. This was treated for a week with concentrated sulphuric acid, allowed to stand several days over sodium, and finally distilled. In this way were obtained four grams of a fraction boiling sharply at 114° under 760 mm. pressure.

Analysis gave the following results:

0.1606 gram substance gave 0.4950 gram CO_2 and 0.2297 gram H_2O.

	Calculated for C_8H_{18}.	Found.
C	84.21	84.05
H	15.79	15.89

Properties.—Liquid, practically odorless, boiling at 114° under 760 mm. pressure. The specific gravity at 15° is 0.7084. The index of refraction $[\pi_D]_{25} = 1.3996$.

Second Method.

Ethyl Ethylisopropylacetacetate,

$CH_3COC(C_2H_5)(CH(CH_3)_2)CO_2C_2H_5$.

—Following Conrad's method[1] for the preparation of ethyl ethylacetacetate from ethyl acetacetate, sodium was dissolved in absolute alcohol and the calculated amounts of ethyl acetacetate and ethyl iodide were added. The solution was boiled until it became neutral, and the small amount of unchanged ethyl iodide was distilled off. In this alcoholic solution of ethyl ethylacetacetate an atom of sodium was dissolved, the calculated quantity of isopropyl iodide was added, the solution boiled until it was neutral, and the ethyl ethylisopropylacetacetate isolated in the usual fashion.

The fractional distillation of the product and the elimination of its impurities was rather difficult, but pure ethyl ethylisopropylacetacetate was obtained by boiling the crude product for four hours with a 10 per cent solution of caustic potash, which decomposed all other acetacetic ester derivatives, forming ketones, while only a small quantity of the principal compound was saponified. On separating the floating layer, drying with potassic carbonate, and distilling, the low boiling ketones were driven off, and after fractionating the residue twice, ethyl ethylisopropylacetacetate distilled constantly at 224° under 760 mm. pressure.

Analysis gave the following results:

0.2041 gram substance gave 0.4895 gram CO_2 and 0.1901 gram H_2O.

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[1] *Loc. cit.*

	Calculated for $C_{11}H_{20}O_3$.	Found.
C	66.00	65.41
H	10.00	10.34

The yield of ethyl isopropylacetacetate was not very good, 135 grams of ethyl acetacetate giving only from 60 to 80 grams. In the above-mentioned purification by caustic potash, the same amount of material gave a few grams of acetone, about two grams of methyl-*n*-propyl ketone, a small quantity of methylisobutyl ketone, and six to seven grams of 3-ethyl-2-pentanone.

Properties of Ethyl Ethylisopropylacetacetate. — Colorless, oily liquid boiling at 224°; has a strong, rather pleasant odor like pine wood; and is miscible with ether, ethyl alcohol, methyl alcohol, benzene, toluene, glacial acetic acid and chloroform.

3-Isopropyl-2-pentanone, $CH_3COCH(C_2H_5)(CH(CH_3)_2)$. — It was found that ethyl ethylisopropylacetacetate was split into the corresponding ketone with great difficulty. By boiling with five molecules of caustic potash in ten per cent solution for sixty hours not over twenty per cent was decomposed. In some experiments the mixture was heated in an autoclave as high as 150°, but this did not better the yield, while in other experiments baric hydrate was found to act even more slowly than potassic hydrate. Increasing the concentration of the alkali brought about no practical improvement, for it caused a greater percentage of acid saponification. In the method adopted, the ester was boiled with five molecules of caustic potash (ten per cent solution) for a week and distilled with steam, and the ketone was separated, dried with calcic chloride and fractionated. The ketone collected in a fraction boiling at 145° to 165° and the unchanged ester at 220° to 225°. The fraction 145° to 165° was refractionated several times, using a long Hempel column, until the major part boiled constantly at 154° under 760 mm. It is rather difficult to get rid of small amounts of impurity which cause it to boil between 152° to 155°. The usual yield of ketone, after a week's boiling, was 25 to 30 per cent of the theoretical. The unchanged ester was recovered and treated with alkali again.

On analysis this ketone, $CH_3COCH(C_2H_5)(CH(CH_3)_2)$, gave the following results:

0.1901 gram substance gave 0.5231 gram CO_2 and 0.2204 gram H_2O.

	Calculated for $C_8H_{16}O$.	Found.
C	75.00	75.03
H	12.50	12.88

Properties.—Colorless liquid; boils at 154° under 760 mm. pressure; has a strong odor very much like camphor; and is miscible with ether, ethyl alcohol, methyl alcohol, benzene, toluene, glacial acetic acid and chloroform.

3-Isopropyl-2-pentanol, $CH_3C(OH)CH(C_2H_5)(CH(CH_3)_2)$. —This carbinol was produced from the corresponding ketone, described above, with sodium and water in presence of ether, by the method given in a previous paper for the reduction of 4-methyl-2-heptanone.[1] The fractionation of the ether residue yielded a liquid boiling at 165° to 175° which, on redistillation, boiled at 172°. This was the 3-isopropyl-2-pentanol.

The yield of carbinol was generally about ninety per cent of the theoretical (25.6 grams of ketone yielded about 23.6 grams of carbinol). No special study was made of the small amount of pinacone which occurred as a by-product.

Analysis of 3-isopropyl-2-pentanol gave the following results:

0.1002 gram substance gave 0.2708 gram CO_2 and 0.1258 gram H_2O.

	Calculated for $C_8H_{18}O$.	Found.
C	73.85	73.72
H	13.85	13.95

Properties.—Colorless, oily liquid; boils at 172° under 760 mm.; has an odor like sour bread; and is miscible with ether, ethyl alcohol, methyl alcohol, benzene, toluene and chloroform.

3-Isopropyl-2-iodopentane, $CH_3C(I)CH(C_2H_5)(CH(CH_3)_2)$, *and its Reduction to Diethylisopropylmethane.*—The preparation and reduction of 3-isopropyl-2-iodopentane was carried out by the same methods and using the same proportions as in the preparation and reduction of 3-ethyl-2-methyl-2-iodopentane already described in this paper, so it is unnecessary to give any further details. Twenty grams of this carbinol gave about 5 grams of the hydrocarbon, a yield of less than 30 per cent of the theoretical.

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[1] Ber. d. chem. Ges., 40, 354.

By this procedure an octane was obtained, which was practically odorless; boiled at 114° under 760 mm. pressure; at 15° had the specific gravity 0.7084; and the index of refraction, determined by a fine Pulfrich refractometer, $[{}^{\pi}{}_{D}]_{5}$ = 1.3996. It therefore agreed perfectly in physical properties with the octane prepared by the method described in the first part of this paper, and there is no doubt that the two are identical in every respect.

The interesting analogies existing between these octanes and two others, the descriptions of which are as yet unpublished, must be reserved for a future paper.

I wish to express my indebtedness to the C. M. Warren Fund for iodine used in this research.

CAMBRIDGE, MASS.,
May 2, 1907.

[Contribution from the Texas Experiment Station.]

THE AMMONIA-SOLUBLE PHOSPHORIC ACID OF THE SOIL.

By G. S. Fraps.

In the course of the investigation of the phosphoric acid of the soil which is being conducted at the Texas Experiment Station, it was considered necessary to study the phosphoric acid which is dissolved by ammonia from the soil after treatment with hydrochloric acid to remove lime. This phosphoric acid, which is dissolved along with the humus of the soil, is termed by some workers humus-phosphoric acid, assumed to be in organic combination and of considerable importance.

The following experiments were designed to throw some light upon the nature and importance of ammonia-soluble phosphoric acid, as we prefer to call it.

Solubility of Mineral Phosphates in Ammonia.

It appeared desirable first to study some mineral phosphates which may occur in the soil to ascertain which one, if any, would give up its phosphoric acid to ammonia under the conditions of the extraction of humus-phosphoric acid.

Method of Work.—The quantity of phosphate containing 0.1 gram phosphoric acid was allowed to remain in contact with 2000 cc. of 4 per cent ammonia for 24 hours, being shaken from time to time.

The mixture was then filtered, 500 cc. of the filtrate evaporated to dryness, taken up with acid and water, and the phosphoric acid determined.

The amount of phosphoric acid used would correspond to 100 grams soil containing 0.1 per cent phosphoric acid in contact with 2000 cc. ammonia, or a ratio of 1 gram soil to 20 cc. ammonia. As the methods of the Association of Official Agricultural Chemists for humus require 50 cc. ammonia to 1 gram soil, the ratio of phosphoric acid to solvent is wider, and therefore the action of the solvent would be greater in the extraction of humus from the soil than in our experiment with mineral phosphates. Our results are given in the following table:

Phosphoric Acid Dissolved by Ammonia, in Percentage of Phosphoric Acid Present.

Ferric phosphate (precipitated)	100
Vivianite (ferrous phosphate)	98
Dufrenite (basic ferric phosphate)	13
Triplite (iron-manganese phosphate)	4
Wavellite (basic aluminium phosphate)	44
Variscite (aluminium phosphate)	18
Apatite	3
Phosphorite	2

Other specimens of these phosphates were examined, with similar results.

It is evident that ammonia dissolves considerable phosphoric acid from iron and aluminium phosphates, and little from the calcium phosphates.

The decomposition of ferric phosphate or vivianite by ammonia is apparent to the eye. The yellow ferric phosphate or black vivianite is converted into red ferric hydroxide, which remains suspended in the liquid.

From this experiment it appears probable that the mineral phosphates of the soil may give up some of their phosphoric acid to ammonia, and also that the inorganic phosphoric acid dissolved in the ammonia is probably of low agricultural value, being derived from iron and aluminium phosphates.

Solubility of Absorbed Phosphoric Acid.

While the preceding experiment shows that some of the ammonia-soluble phosphoric acid is probably of mineral origin, it does not prove that this is the case. We have accordingly made experiments to see if the phosphoric acid absorbed by the soil is soluble in ammonia. That is, we have determined the ammonia-soluble phosphoric acid, according to the methods for humus, in soils before and after they were treated with a known quantity of potassium phosphate. An increase in the ammonia-soluble phosphoric acid (or so-called humus-phosphoric acid) can only be due to the absorbed phosphoric acid, and such an increase would be evidence that a portion of the ammonia-soluble phosphoric acid of an ordinary soil is derived from inorganic phosphates.

Method of Study.—Twenty grams soils were brought in contact with 100 cc. potassium phosphate solution containing 0.2 gram phosphoric acid. After 24 hours, the solution was poured off, the soil treated, first with 1 per cent hydrochloric acid to remove lime, then with water to remove acid, and finally with 4 per cent ammonia. The ammonia solution was made up to 1000 cc. and 100 cc. were used for the determination of phosphoric acid.

At the same time, another portion of the soil was treated with water in place of potassium phosphate, and the experiment carried out exactly as before.

None of the soils used was rich in humus. Soils 336, 341, 821, 823 and 825 contained little or no humus.

The results of the experiment are as follows:

Per cent of Ammonia-Soluble Phosphoric Acid in the Soil.

		Treated with phosphate.	Treated with water.	Gain (+) or Loss (—).
134	San Antonio loam	0.035	0.028	+0.007
326	Crawford clay	0.081	0.081	+0.000
330	Colton stony clay	0.093	0.086	+0.007
336	Lufkin fine sandy loam	0.073	0.015	+0.058
341	Susquehanna fine sandy loam (subsoil)	0.059	0.028	+0.031
829	Houston loam	0.059	0.039	+0.020
324	Houston black clay	0.065	0.039	+0.026
816	Laredo fine sand	0.036	0.025	+0.011
817	Lufkin fine sandy loam	0.036	0.029	+0.007
821	Orangeburg fine sand	0.034	0.019	+0.015
823	Orangeburg fine sandy loam (subsoil)	0.228	0.060	+0.168
825	Lufkin fine sandy loam	0.048	0.028	+0.020

It is evident that the absorbed phosphoric acid is soluble in ammonia. It follows, then, that a portion of the so-called humus-phosphoric acid is of mineral origin, and that an increase in the amount of it in the soil during the decay of vegetable matter or from other causes does not necessarily mean that a gain of organic phosphoric compound has taken place.

Soil 823, which contains practically no humus, contains as much humus-phosphoric acid, so-called, as the average of seven Minnesota soils rich in humus.

Distribution of Ammonia-Soluble Phosphoric Acid.

The ammonia-soluble phosphoric acid derived from the soil may be divided in three portions:

(1) The phosphoric acid associated with the clay held in suspension in the liquid.

(2) That precipitated with the organic matter when the liquid is neutralized with acid.

(3) The portion which remains in solution. It is a comparatively easy matter to separate the phosphoric acid into these three parts. We precipitated the clay by the addition

of ammonium sulphate in the proportion of one-half gram to 100 cc. After filtering off the precipitate and washing it several times with ammonium sulphate of the strength indicated above, the organic matter was precipitated by making the liquid slightly acid. The precipitate was collected on a filter and washed. Phosphoric acid is determined in the two precipitates and that in solution is estimated by difference, the total phosphoric acid being determined in the original solution.

The precipitation of the organic matter is not complete. Some of it remains in solution. The distribution between these groups of the phosphoric acid of some soils is given in the following table:

Percentage of Ammonia-Soluble Phosphoric Acid in the Soil.

	In clay precipitate.	In organic precipitate.	In filtrate.	Total.
741	0.005	0.021	0.042	0.068
742	0.005	0.020	0.034	0.059
743	0.008	0.019	0.016	0.043
744	0.0012	0.020	0.034	0.066
745	0.009	0.022	0.042	0.073
746	0.001	0.023	0.052	0.076
747	0.010	0.020	0.025	0.055
Average,	0.007	0.021	0.036	0.063

These soils were from Minnesota, containing 3 to 6 per cent of humus. They were kindly sent to us by Prof. Harry Snyder.

It appears that on an average 1/9 of the total ammonia-soluble phosphoric acid is in the clay precipitate, 3/9 in the organic precipitate, and 5/9 remains in the filtrate. In dealing with these small quantities, the error of analysis is of course large in comparison with the amount of phosphoric acid present. It appears from our analyses of humic acid, prepared and precipitated in quantity, that the amount of phosphoric acid which is precipitated with the organic matter is smaller than is indicated above.

Nature of Ammonia-Soluble Phosphoric Acid.

Clay Precipitate.—The phosphoric acid in the clay precipitate probably exists for the greater part in the clay particles, and is not in solution at all. This appears probable when we consider, first, that the finer portion of the soil always contains phosphoric acid, and second, that there is no reason to believe that phosphates would be precipitated from solution by addition of 0.5 per cent ammonium sulphate. There is, of course, the possibility that some of the phosphoric acid may be mechanically absorbed by the precipitate, but it is hardly likely that more than a small percentage of the total quantity present is held in this way. Otherwise we would expect a clay soil to retain a considerable portion of its ammonia-soluble phosphoric acid when treated with ammonia.

Organic Precipitate.—The phosphoric acid in the organic precipitate is very likely in organic combination.

In the first place, phosphates of iron or aluminium are soluble in acid and would hardly be precipitated when the ammoniacal liquid is made acid.

In the second place, the organic precipitate does not appear to have the power of absorbing phosphates. We dissolved 1 gram of the organic precipitate in ammonia, and added 0.02 gram phosphoric acid in the form of potassium phosphate, and reprecipitated with acid. The organic substance contained 0.0027 gram phosphoric acid and the precipitate the same quantity, which shows that no absorption had taken place. Hence it is not probable that the organic precipitate holds absorbed phosphoric acid.

We also dissolved some of the organic precipitate in ammonia, precipitated with lime, and washed. We removed lime with hydrochloric acid, dissolved the residue in ammonia, and reprecipitated with acid. The dried material was subjected to analysis. The original material contained 0.27 per cent phosphoric acid, the purified material 0.32, thus showing little change in this ingredient. We subjected 1 gram to diffusion. In 24 hours eight per cent of the organic matter passed through, but no phosphoric acid.

We conclude, from these experiments, that the phosphoric acid precipitated with the organic matter after the removal of the clay is in organic combination.

The Filtrate.—It appears probable that most of the phosphoric acid in the filtrate from the precipitation of humus with acid is in inorganic forms, although a small percentage of it may be in organic combination, since the organic precipitate is soluble in water. We have shown that the inorganic phosphoric acid absorbed by the soil is soluble in ammonia, and therefore some of the ammonia-soluble phosphoric acid must be of inorganic origin. There is no evidence that the phosphoric acid in the filtrate is in organic combination. It is probably derived from iron and aluminium phosphates.

Significance of Organic Phosphoric Acid.

We have prepared the organic precipitate from a variety of soils, and found it to contain from 0.15 to 0.54 per cent phosphoric acid. A soil containing 5 per cent humus may thus contain 0.008 to 0.022 per cent of phosphoric acid in organic combination. We found about 0.020 per cent in Minnesota soils which contain good percentages of humus.

The amount of phosphoric acid in organic combination is thus decidedly less than has been assumed from the analysis of the ammonia solution. It is hardly of any value to plants until the phosphoric acid has been released through the decomposition of the organic matter. This decomposition takes place slowly, and the most important product is available nitrogen, which is produced in about ten times the quantity of phosphoric acid released.

The organic phosphoric acid can only be regarded as a reserve store, of value according to the rate at which it decomposes. In soils containing moderate amounts of humus, it can have little importance. In soils containing large quantities of humus, it remains to be demonstrated whether phosphoric acid in this form is or is not of more value than phosphoric acid in other reserve forms.

Summary and Conclusions.

1. Mineral phosphates, especially phosphates of iron and

aluminium, give up phosphoric acid to ammonia under conditions similar to the treatment of the soil with this solvent.

2. Absorbed phosphoric acid left after treatment of the soil with acid is partly soluble in ammonia.

3. A portion of the so-called humus-phosphoric acid must be of inorganic origin; and an increase of ammonia-soluble phosphoric acid during the decay of organic matter in the soil is not evidence that there is a gain of organic phosphoric acid.

4. About 1/9 of the ammonia-soluble phosphoric acid of some Minnesota soils is associated with the clay, 1/3 is associated with the organic matter, and 5/9 remains in solution.

5. The phosphoric acid associated with the organic matter does not diffuse and the amount of it does not increase when the organic matter is precipitated in the presence of phosphoric acid, nor does it decrease when the organic matter is dissolved, precipitated with lime, the lime removed, the precipitate dissolved in ammonia, and reprecipitated. We conclude that the phosphoric acid is in organic combination.

6. The phosphoric acid with the clay is probably not in solution; that in the filtrate is probably for the most part of inorganic origin, derived from iron and aluminium phosphates.

7. The organic phosphoric acid is in much smaller quantity than has been believed to be the case, and therefore of less agricultural significance.

The author wishes to acknowledge the assistance of Messrs. N. C. Hamner and S. E. Asbury, who performed the analytical work.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STUDIES IN CATALYSIS.[1]

V. THE CATALYSIS OF IMIDOESTERS.

By William McCracken.[2]

When the hydrochloride of an imidoester is dissolved in water, it is rapidly decomposed by the water into ammonium chloride and an acid ester according to the formulation,

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[1] Articles I.–IV., This Journal, **39**, 29, 166, 402, 437.

[2] This work was begun in 1898–9 (This Journal, **26**, 209), completed, written and accepted as a dissertation in 1905 and sent to the editor in September, 1907.

$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \rightarrow C_6H_5COOC_2H_5 + NH_4Cl \quad (1).$$

It was early observed that the decomposition appeared to proceed fastest with the salts of those imidoesters which presumably form the weaker bases; for instance, the hydrochloride of ethyl imido-*m*-nitrobenzoate is decomposed very much more rapidly than that of ethyl imidobenzoate. From my own preliminary experiments I found that in one hour 17.44 per cent of the latter was decomposed, while of the former, in the same time and under the same conditions, 8.17 per cent was changed. As all the imidoesters are weak bases and their salts are consequently more or less hydrolyzed by water in proportion to the weakness of the base,

$$C_6H_5C(:NH_2Cl)OC_2H_5 + H_2O \rightleftarrows C_6H_5C(:NH_2OH)OC_2H_5 + HCl \quad (2),$$

it appeared that there might be some connection between the two facts—the relative weakness of the base, as revealed in (2), and the relative velocity of the decomposition shown in (1).

The study of the decomposition of imidoester salts by water was undertaken by me at the suggestion and under the direction of Professor Stieglitz, with the particular object of ascertaining what component of the hydrolyzed mixture, salt or free base, suffers decomposition by water into ester and ammonia, and of determining whether there is any general relation between the velocity of the decomposition of the salts and the affinity constant of the bases, as has just been explained. The study forms part of the investigations on catalysis carried out in this laboratory, and the theoretical and mathematical presentation of the problems involved will be found in the recent papers by Professor Stieglitz[1] on this subject.

I. THE METHODS OF ANALYSIS.

The experimental treatment of the subject under investigation resolved itself into two lines of work. It was necessary, first, to devise methods for following the velocity of reaction

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[1] THIS JOURNAL, *loc. cit.*

(1) quantitatively at a given temperature, and, in the second place, to determine the hydrolysis constants of the salts used. The course of reaction (1) was followed by two different analytical methods. Imidoesters are readily converted into bromimidoesters[1] by the action of hypobromous acid or of bromine and alkalis:

$$C_6H_5C(:NH)OC_2H_5 + HOBr \longrightarrow C_6H_5C(:NBr)OC_2H_5 + H_2O \quad (3).$$

The resulting bromimidoesters are compounds which are difficultly soluble in water and readily extracted by organic solvents; and they are also very readily reduced back to imidoesters by the action of hydriodic acid, iodine being liberated quantitatively according to the formulation

$$C_6H_5C(:NBr)OC_2H_5 + 2HI \longrightarrow C_6H_5C(:NH_2Br)OC_2H_5 + 2I \quad (4).$$

These reactions formed the basis of the first analytical method used; at certain time intervals a measured amount, 25 cc. as a rule, of the solution under investigation was brought into a 250 cc. "Squibb" separatory funnel, 15 cc. of carbon tetrachloride was added, then excess of bromine, and finally 10 per cent sodium hydroxide with vigorous shaking, until the carbon tetrachloride retained but a slight greenish tint. The carbon tetrachloride containing the bromimidoester was then filtered through a paper wet with carbon tetrachloride and the solution extracted again with 10 and 5 cc., respectively, of carbon tetrachloride. To the extracts collected in a glass-stoppered bottle were then added 15 cc. of a 25 per cent solution of potassium iodide and 10 cc. of dilute hydrochloric acid, and the free iodine titrated with N/10 thiosulphate.

The only difficulty met with in the application of the method consisted in the determination of the point at which the excess of bromine used in converting the imidoester into the bromimide is just removed by the addition of alkali, considerable excess of alkali reversing reaction (3) and resulting in a loss of bromimide. Prolonged practice with weighed quantities of the imidoester salt made it possible to determine with considerable accuracy, by the tint of the carbon tetrachloride layer, at which point the excess of bromine is removed without a loss of bromimidoester. The following results of blank experiments with the hydrochloride of ethyl imidobenzoate show the degree of accuracy of the method:

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[1] Stieglitz: This Journal, 18, 761 (1896).

Salt used, gram.	cc. N/10 thiosulphate required.	cc. N/10 thiosulphate calculated.
0.2415	26.19	26.15
0.1144	12.37	12.33
0.2080	22.26	22.43

The second analytical method, developed in the investigations of Stieglitz and Derby,[1] is far easier and more reliable in execution than the bromine method and eliminates the personal factor involved in judging a tint. The degree of accuracy is shown by the blank experiments of Stieglitz and Derby, as well as by the following determinations made by myself with imidoester salts which they did not use.

The Hydrochloride of Isoamyl Imidobenzoate.

Substance used, gram.	cc. N/10 NaOH calculated.	cc. N/10 NaOH found.
0.2360	10.38	10.37
0.2947	12.95	12.95
0.2277	10.01	10.03

The Hydrochloride of Isobutyl Imidobenzoate.

Substance used, gram.	cc. N/10 NaOH calculated.	cc. N/10 NaOH found.
0.2520	11.80	11.82
0.2454	11.49	11.47

The Hydrochloride of Ethyl Imido-p-toluylate.

Substance used, gram.	cc N/10 NaOH calculated.	cc. N/10 NaOH found.
0.3630	18.18	18.13
0.3214	16.10	16.02

Analyses were also made of the hydrochloride of isoamyl imidobenzoate in the presence of added ammonium chloride to see if it affected the method. The following results were obtained, 0.1 and 0.5 equivalents, respectively, of ammonium chloride being used:

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[1] THIS JOURNAL, **39**, 437.

Substance used, gram.	cc. N/10 NaOH calculated.	cc. N/10 NaOH found.
0.2301	10.11	10.18
0.2280	10.02	10.03

These results show that the presence of ammonium chloride does not affect the method.

The reliability of the analytical method used with each salt of an imidoester was tested in every instance with the salt itself.

The experimental determinations of the hydrolysis constants of equation (2) and the affinity constants of the imidoesters were made by the conductivity method of Walker[1] and of Bredig,[2] the degree of hydrolysis being ascertained by the equation

$$x = \frac{M_{obs} - \Lambda_s}{\Lambda_{HCl} - \Lambda_s},$$

where x is the percentage of free base and acid liberated by hydrolysis, M_{obs} is the observed molecular conductivity, and Λ_s and Λ_{HCl} are the molecular conductivities of the non-hydrolyzed salt and of hydrochloric acid, respectively, for the concentration used.[3] Since a solution of the salt (equation 2) is continually decomposing according to (1) from the first moment that the water touches it, it was necessary to ascertain the conductivity, M_{obs}, for the unchanged solution ($t = 0$) from the results of a series of readings made at stated time intervals. The conductivity changed slowly in most cases under investigation and a simple method of extrapolation, based on the observed conductivities without regard to the velocity constants[4] of reaction (1), was found to be sufficiently accurate. The method of extrapolation used will be explained in connection with some of the data found in the next part. In two or three cases (ethyl imido-*m*-nitrobenzoate and the imidoesters of phenylacetic acid), the velocity of decomposition proved to be so great that a double method of extrapolation had to be resorted to (p. 605) in order to find M_{obs}, and the constants obtained in some cases are considered to be, at best, approximations.

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[1] Z. physik. Chem., **4**, 319 (1889).

[2] *Ibid.*, **13**, 289 (1894).

[3] Stieglitz and Derby: THIS JOURNAL, **31**, 449 (1904).

[4] Stieglitz and Upson: THIS JOURNAL, **31**, 458 (1904).

The molecular conductivities, Λ_s, of the nonhydrolyzed salts were measured by Bredig's method, the conductivity being determined in the presence of sufficient free base added to the salt solution to overcome the hydrolysis, without, at the same time, having enough free base present to affect the measurement. In this case, too, decomposition according to (1) occurred continually and the values for Λ_s were found by extrapolation from a series of readings, exactly as in the case of M_{obs} for the hydrolyzed salt.

From the degree of hydrolysis, x, the hydrolysis constants, K_{hydr}, and the affinity constant, k_{base}, were calculated in the usual way according to the Walker-Arrhenius equation for hydrolyzed salts:

$$\frac{C_{salt}}{C_{base}\,C_{acid}} = \frac{k_{base}}{k_w} = K_{hydr} \qquad (7),$$

where C_{salt}, C_{base} and C_{acid} signify the concentrations of salt, base and acid in gram molecules per liter, and k_w is the ion product for water (1.2×10^{-14} at 25°).[1] If one gram molecule of salt is used in V liters, we have

$$\frac{V(1-x)}{x^2} = \frac{k_{base}}{k_w} = K_{hydr} \qquad (8).$$

II. EXPERIMENTAL PART.

1. *The Hydrochloride of Ethyl Imidobenzoate.*

The hydrolysis constant for the hydrochloride of ethyl imidobenzoate and the affinity constant for the base were determined by Stieglitz and Derby[2] as follows:

$$K_{hydrolysis} = 9.1 \times 10^5. \ k_{base} = 10.9 \times 10^{-9}.$$

The velocity of the decomposition of the salt by water was determined by me in a series at 25° (±0.01).[3]

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[1] Van't Hoff's "Lectures on Theoretical and Physical Chemistry," 1, page 133.

[2] *Loc. cit.*

[3] In a few earlier experiments the variations were sometimes 0°.05 to 0°.1. The exact temperature will be given in each case.

In the following table, columns 1 and 5 give the time in minutes, and columns 2 and 6 the cc. of N/10 thiosulphate required for 25 cc. of the salt solution. These volumes are proportionate to the concentration $(C - x_t)$ at any moment t and are used in calculating the constant according to the equation for a monomolecular reaction,[1]

$$k_{salt} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (9).$$

Columns 3 and 7 give the constants calculated according to this equation. In all the experiments the concentration of the salt was 0.05 molar.

Table I.

t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.	Temp.	t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.	Temp.
0	25.00	1.34		60	20.57	1.41	
60	20.78	1.36	25°.1	120	16.77	1.45	25°
120	17.16	1.35		180	14.16	1.37	
180	14.26	1.39		240	11.65	1.38	
240	11.60						
60	20.60	1.40		180	13.58	1.41	25°.08
120	16.83	1.43	25°.05	360	8.09	1.36	
180	14.17	1.37					
240	11.80	1.36					
60	20.63	1.39		180	14.15	1.41	25°.08
120	16.92	1.41	25°.08	360	8.27	1.35	25°.08
180	14.39	1.33					
240	11.88	1.35					

Mean: $434.3\ k_{salt} = 1.384$; $k_{salt} = 0.00319$.

These results show that the velocity of the reaction is proportionate to the concentration of the salt present in the solution of the hydrolyzed imidoester salt (equation 2). The velocity constants, k_b, were also calculated for a reaction supposed to proceed with a velocity proportionate to the concentration of the free base[2] present at any moment according to the combined equations (1) and (2). If the reaction velocity of the equation (1) were proportionate to the concentration of the free base, we would have[1]

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[1] The salt is so little hydrolyzed according to (2) that k represents almost exactly the velocity of decomposition as being proportionate to the concentration of the salt. See Stieglitz: *Loc. cit.*

[2] See Stieglitz and Upson: This Journal, **31**, 458 (1904).

$$k_b = \frac{2}{t_2 - t_1}\sqrt{\frac{K_{hydr}}{V}}\left[\sqrt{1 - x_1} - \sqrt{1 - x_2}\right] \qquad (10),$$

in which K_{hydr} is the hydrolysis constant of equation (2) and V the volume in which one gram molecule of salt is dissolved.

The first two series of Table II. give the values for k_b calculated according to this equation for the decomposition of the salt in a 0.05 molar solution. As was to be expected, the values are not constant. As a farther test of this point, the velocity of decomposition was also determined in solutions of the imidoester salt containing a known excess of free base, thus permitting of a greater variation in the concentrations of the base. If the velocity of decomposition of an imidoester into ammonia and an acid ester were proportionate to the concentration of the free base present, then for a mixture of the salt and an added excess of free base we would have

$$\left\{\begin{aligned} k_{base} = \frac{1}{K_v(t_2 - t_1)}&\Big[\sqrt{R - 4K_v x_1} - \sqrt{R - 4K_v x_2} \\ &+ (1 - s - K_v)\log\text{nat}\,\frac{\sqrt{R - 4K_v x_2} + (1 - s - K_{v,}}{\sqrt{R - 4K_v x_1} + (1 - s - K_v}\Big] \end{aligned}\right. (11),$$

in which $K_v = V/K_{hydrolysis}$ and $R = (1 - s + K_v)^2 + 4K_v s$. One gram molecule of imidoester (base and salt) is used in V liters; s gives the percentage of one gram molecule of salt present; $1 - s$, the percentage of one molecule of base. The volume V was always 20 liters in these experiments. The last two series of Table II. give the results.

Table II.

t.	cc. N/10 thiosulphate.	*kbase.*		*t.*	cc. N/10 thiosulphate.	*kbase.*	
60	20.78	0.63		180	14.14	0.149	25°.04
120	17.16	0.61	25°.1	360	8.21	0.115	$s = 0.984$
180	14.26	0.58	$s = 1$				
240	11.60	0.53					
60	20.60	0.66		180	14.37	0.0481	25°.04
120	16.83	0.64	25°.05	360	8.25	0.0384	$s = 0.950$
180	14.17	0.59	$s = 1$				
240	11.80	0.47					

---

[1] Stieglitz: *Loc. cit.* The formula is simplified from the rigorous expression as explained in the above paper.

It is certain, therefore, that the reacting substance in the formation of an ester and ammonia is not the free base, as was at one time thought possible, but rather the salt or its positive ion. This conclusion was confirmed by the results obtained in the presence of an added excess of hydrochloric acid. Although a small excess of acid practically eliminates all the free base formed by hydrolysis, owing to the large value of the hydrolysis constant, the velocity of the reaction remains practically unchanged in the presence of the small excess of acid.

A larger excess of acid reduces the velocity considerably. As in dilute solutions the salt is very largely dissociated into its ions, it was thought from the beginning that the real reacting substance is the positive ion only[1] and that the true velocity constant would show a reaction proceeding directly proportionate only to the concentrations of the positive salt ion present and not to the total salt concentrations. The addition of an excess of acid, by increasing the total electrolyte concentration, decreases the degree of ionization according to Arrhenius' principle of isohydric solutions. When this work was first carried out it was intended to assume provisionally in our calculations that the degree of ionization of the hydrochloride of ethyl imidobenzoate would correspond approximately to that of ammonium chloride in similar concentrations. Since then Dr. Schlesinger[2] has determined directly the degrees of ionization of the imidoester salts and we are indebted to him for the use of his values for α in the following calculations. Schlesinger has shown, in the work on the velocity of decomposition of the imidoester salts in solutions of varying concentrations, that, the velocity being put proportionate to the concentration of the positive ester ions, there is an accelerating "salt effect" corresponding to the like effect of electrolytes on the catalysis of cane sugar, methyl acetate, etc. We have included the consideration of this effect also in the analysis of the experimental data on the velocity of decomposition of ethyl imidobenzoate in the presence of an excess of hydrochloric acid. In Table III. are given the data of these determinations, all of which were carried out with 0.05 molar ethyl imidobenzoate and varying amounts of hydrochloric acid. The first three columns have the same significance as in Table I. In columns 4 and 8 the excess of acid used is given in moles per liter, and the exact temperature for each experiment is given in the same column. 25 cc. were used for each titration, and when $t = 0$ these require 25 cc. N/10 thiosulphate. The constants are calculated according to the logarithmic function (equation 9),

---

[1] *Vide* Stieglitz.

[2] See a later article in THIS JOURNAL.

$$K = \frac{1}{t} \log \text{nat} \frac{25}{v_t},$$

in which v_t represents the cc. thiosulphate used at the moment t.:

Table III.

t.	cc. N/10 thiosulphate.	434.3 × k_{salt}.	Acid (temp.).	t.	cc. N/10 thiosulphate.	434.3 × k_{salt}.	Acid (temp.).
180	14.08	1.385	0.05	60	21.00	1.260	
360	7.97	1.380	25°.00	120	17.78	1.235	0.25
180	14.15	1.373	0.05	180	15.00	1.233	25°.03
360	8.04	1.370	25°.05	240	12.61	1.240	
180	14.42	1.330	0.10	60	21.37	1.133	0.5
360	8.46	1.308	25°.00	120	18.21	1.147	25°.05
180	14.34	1.341	0.10	180	15.67	1.127	
360	8.37	1.320	25°.01	240	13.46	1.122	
120	17.62	1.267	0.25	60	21.95	0.942	
180	14.94	1.241	25°.03	120	19.31	0.935	1.00
240	12.71	1.225		180	17.00	0.931	25°.00
				240	15.17	0.904	

In Table IV. (p. 598) the analysis of the data is given. Column 1 in the table gives the moles of hydrochloric acid used in excess with the 0.05 molar solution of ester salt. In column 2 are given the estimated concentrations of the imidoester solutions whose degree of ionization would correspond to that of the imidoester salt as affected by the presence of the added acid; these concentrations are calculated on the basis of the theory of isohydric solutions, that the salt and acid may be supposed to share the water present in such proportions that the concentration of the common ion $(\overline{\mathrm{Cl}})$ becomes the same for the acid and the salt in their respective parts of the solution;[1] then, when such solutions are mixed in any proportions there is practically no change in the degree of ionization of the electrolytes. In making this estimation, the difference in the degree of ionization of the acid and salt in equimolar solutions was taken into consideration, that of the salt (Schlesinger) being unusually low. In line 2, for instance, if the salt and acid ionized approximately equally, the ionization of the salt would be referred, as usual, to a salt solution equimolar to the total electrolyte concentration (0.05 + 0.05 or 0.1 molar), but the difference in the degree of ionization of the salt and the acid makes it necessary to consider the water divided in about the ratio of 0.53 part for the acid and 0.47 part for the salt, and (0.05/0.47) gives 0.106 as the concentration of the isohydric salt solution. The correction here is very slight but, as will be seen in the table, it is quite considerable for the stronger acid solutions; for 0.5 molar acid, for instance, we have a partition of the water in about the ratio 0.94:0.06 (instead of 0.91 to 0.09) to secure isohydric solutions, and the salt solution is then 0.8 molar instead of 0.55.

In column 3, the degree of ionization of the salt is given corresponding to the molar concentration given in column 2; the values are obtained by interpolation from Dr. Schlesinger's determinations.

In column 4, the observed velocity constant, k_{salt}, is given, as reported in Table III., for each experiment. In column 5, the velocity of the reaction is referred to the concentration of the positive salt ion according to the equation

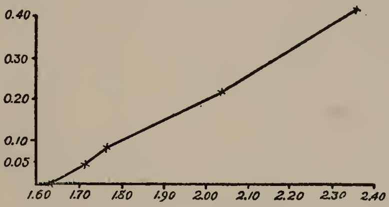
$$K_{ion} = \frac{k_{salt}}{\alpha} \qquad (13).$$

The values in this column show very markedly the large accelerating effect of the hydrochloric acid, or, rather, of its ions.[2] If the action is really subject to this effect, the effect should be, as usual, directly proportionate[1] to the concentration of the ions of the acid;[2] in other words, the velocity should be a rectilinear function of these concentrations. The accompanying diagram shows that, as a matter of fact, if we plot the concentrations of the acid ions ($m \times \alpha_{HCl}$ of columns 1 and 6 in the table) as ordinates and the velocities K_{ion}, *i. e.*, K_{salt}/α, as abscissas we do get a very nearly straight line.

---

[1] Arrhenius: Z. physik. Chem., **2**, 286 (1888).

[2] This accelerating "salt effect," it may be recalled, is generally ascribed to the influence of the salt ions on the dissociation or active mass of water [Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889); and Euler: *Ibid.*, **32**, 348 (1900)] which enters into the action under investigation, as shown in equation (1). See Stieglitz: THIS JOURNAL, articles I. and II., *loc. cit.*



By taking, from the diagram, the acceleration as $\frac{0.73}{0.42 \times 1.63}$ or 1.07 per gram ion of hydrogen (the concentration of hydrogen ions is proportionate, of course, to the total concentrations of ions obtained from hydrochloric acid) we can calculate, for each experiment, the velocity with which it ought to proceed if our theory is correct. The observed velocity, $434{\cdot}3\ k_{salt}$, should correspond to the calculated velocity, $434{\cdot}3\ k_{salt\ calc.}$, found as follows:

$$434{\cdot}3\ k_{salt\ calc.} = \frac{1.384 \times \alpha_{salt} \times (1 + 1.07\ m_{HCl} \times \alpha_{HCl})}{0.846} \quad (13),$$

in which 1.384 is the velocity in absence of any acid; 0.846, the degree of ionization for this condition; α_{salt}, the degree of ionization of the salt given in column 3; m_{HCl}, the concentration of the added acid (column 1); and α_{HCl}, the degree of ionization of the acid as calculated from the conductivities for concentrations equal to the total electrolyte concentrations. Column 6 gives α_{HCl}, and column 7 the calculated constant, 434.3 $k_{salt\ calc}$.

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[1] Arrhenius: *Loc. cit.*

[2] The effect of the ions of the 0.05 mole of salt present (see Schlesinger's paper) is so small, compared with that of the acid, that it was neglected.

Table IV.

1	2	3	4	5	6	7
m_{acid}.	Est salt.	100 α_{salt}.	434.3 k_{salt}	$\frac{434.3\ k_{salt}}{\alpha_{salt}}$.	100 α_{HCl}.	434.3 × $k_{calc\ salt}$.
0.00	0.05	84.6	1.384	1.63	0.00	1.384
0.05	0.106	80.0	1.372	1.72	91.4	1.374
0.05	0.106	80.0	1.383			
0.10	0.167	74.7	1.319	1.77	90.9	1.340
0.10	0.167	74.7	1.330			
0.25	0.4	61.0	1.242	2.04	87.5	1.231
0.25	0.4	61.0	1.244			
0.50	0.8	(48.0)	1.132	2.36	84.3	1.139

The comparison of the last column, $k_{calc\ salt}$, with the fourth column, giving the experimental values for k_{salt}, shows how close the agreement is between the two values in all the concentrations used.

We may conclude, therefore, that this series of experiments confirms the result established by Stieglitz and Schlesinger that the decomposition of salts of imidoesters according to the equation (1) is a reaction of the positive salt ions, proceeding proportionate to their concentrations, and subject to an acceleration by the so-called "salt effect" proportionate to the electrolyte used,[1] presumably owing to an effect on the active mass of water, the other agent in the action (see equation 1). The reaction should, therefore, more properly be represented as follows:[2]

$$C_6H_5C(\overset{+}{N}H_2)OC_2H_5 + HOH \longrightarrow C_6H_5CO_2C_2H_5 + \overset{+}{N}H_4 \quad (1').$$

2. The Hydrochloride of Isobutyl Imidobenzoate.

The hydrolysis constant (equation 2) for isobutyl imidobenzoate was determined by conductivity measurements of the salt solution in the absence and presence of a slight excess of the free base. As the salt undergoes continuous change in the solution, the conductivities for $t = 0$ were ascertained by a process of extrapolation which will be illustrated by the data for the experiments with 1/32 and 1/64 molar salt solutions. For the sake of brevity, the like data for all later experiments will be omitted.

---

[1] A more extensive, rigorous investigation of the "salt effect" is being carried out by Miss Edith Barnard. The above results are merely preliminary.

NOTE: Dr. McCracken's article was written in 1905, Dr. Barnard's work completed in 1907.—J. S.

[2] Stieglitz: *Loc. cit.*

The measurements were made with a Kohlrausch bridge at 25° (±0.01) in an Arrhenius cell. The water used had a specific conductivity of 4×10^{-6}, for which a correction was made only in the neutral solutions in the presence of the added base, but not in the case of the acid-reacting hydrolyzed salt solutions. The conductivities are given in reciprocal ohms.

In the following table, V., we have in columns 1 and 5 the time in minutes; in columns 2 and 6, the observed specific conductivities; in columns 3 and 7, the difference in these for 5 minute intervals. In columns 4 and 8 the extrapolated values for the *original* specific conductivities are given.

Table V.

1/32 molar.

t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_o$.	t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_o$.
0	....	..	(2741)	15	2826	23	2740
5	2769	..	2741	20	2852	26	2738
10	2803	34	2746	25	2883	31	2740
					Mean,	28.5	2741

The mean specific conductivity calculated for $t = 0$ is 0.002741: the molecular conductivity is therefore 87.7.

2. 1/64 molar.

i.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_o$.	t.	$10^6 \times \kappa$.	Δ.	$10^6 \times \kappa_o$.
0	....	..	(1442)	15	1482	13	1442
5	1455	14	1442	20	1497	15	1443
10	1469	..	1445	25	1509	12	1441
					Mean,	13.5	1442

In Table VI. a summary of the data is given for the estimation of $K_{hydrolysis}$. The calculation is made according to the Arrhenius-Walker method.[1]

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[1] Page 591.

Table VI.

V.	M_v.	Λ_v.	$100x$.	$10^{-5} K_{hydrolysis}$.
32	87 70	85.82	0.612	8.5
32	87.25	85.82	0.466	15.0
64	92.29	89.73	0.828	9.3
64	92.16	89.73	0.786	10.3
128	97.40	93.47	1.28	7.8
256	100.40	95.82	1.49	11.3

Mean: $K_{hydrolysis} = 10.4 \times 10^5$; $k_{base} = 12.5 \times 10^{-9}$.

In Table VII. are given the results of the determination of the velocity of decomposition of the hydrochloride by water at 25° (±0.01°). The constant, k_{salt}, is calculated according to equation (9). 25 cc. of the salt solution was used for each titration. V gives the volume containing 1 gram molecule of salt.

Table VII.

1. $V = 30$.

t.	cc. N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc. N/10 NaOH.	$434.3 \times k_{salt}$.
0	8.33	....	200	4.51	1.33
10	8.02	(1.65)	260	3.80	1.31
40	7.40	1.29	320	3.19	1.30
140	5.40	1.34			

Mean: $434.3\ k = 1.315$; $k = 0.00303$.

2. $V = 20$.

t.	cc. N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc. N/10 NaOH.	$434.3 \times k_{salt}$.
0	12.50	....	130	8.498	1.29
10	12.13	1.31	160	7.76	1.29
40	11.10	1.29	190	7.14	1.28
70	10.19	1.27	340	4.58	1.28
100	9.28	1.29	370	4.20	1.28

Mean: $434.3\ k = 1.287$; $k = 0.00296$.

For k_{ion} we have $k_{ion} = k_{salt}/\alpha$, or, for the 1/30 molar solution,[1]

$$k_{ion} = \frac{0.001315}{0.4343 \times 0.876} = 0.003456,$$

and for the 1/20 molar solution

$$k_{ion} = \frac{0.001287}{0.4343 \times 0.846} = 0.003502.$$

---

[1] α was taken to be the same for the isobutyl ester as found by Schlesinger for the ethyl ester.

3. *The Hydrochloride of Isoamyl Imidobenzoate.*

The following table, VIII., gives the data for the calculation of the hydrolysis constant:

Table VIII.

V.	M_v.	Λ_v[1].	$100x$.	10^{-5} $K_{hydr.}$
32	88.46	86.7	0.579	9.6
64	91.90	89.6	0.745	11.5
128	95.23	92.41	0.912	15.2
256	98.84	95.33	1.14	19.4

Mean, 14.0×10^5.

For the affinity constant we have $k_{base} = 17 \times 10^{-9}$.

In Table IX. we have the results of the determinations of the velocity of decomposition of the hydrochloride in water at 25° (±0.01°). The values in this table are obtained in the same way as those in Table VII., and the columns have the same significance.

Table IX.

1. $V = 20$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
0	12.5	....	120	8.78	1.27
10	12.1	(1.41)	180	7.40	1.27
60	10.49	1.27	240	6.09	1.30

Mean: $434.3\ k = 1.278$; $k = 0.00294$.

2. $V = 20$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
0	12.50	....	160	7.80	1.28
10	12.09	(1.45)	199	6.98	1.27
40	11.08	1.31	320	4.92	1.27
80	9.76	1.34	360	4.32	1.28
120	8.74	1.29	400	3.94	1.25

Mean: $434.3\ k = 1.287$; $k = 0.00296$.

3. $V = 10$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
0	25.00	....	174	15.22	1.24
14	24.15	(1.08)	214	13.62	1.23
54	21.44	1.24	334	9.82	1.22
94	19.19	1.22	374	8.71	1.22
134	17.05	1.24	404	8.03	1.22

Mean: $434.3\ k = 1.229$; $k = 0.00283$.

---

[1] N/80 free base was used.

For k_{ion} we have, for the 1/20 molar solution, $k_{ion} = 0.003491$. For the 1/10 molar solution, $k_{ion} = 0.003505$.

4. *The Hydrochloride of Ethyl Imido-p-toluylate.*

In the next table will be found the calculations of the hydrolysis constant of this substance at 25° (±0.01).

Table X.

V.	M_v.	Λ_v.[1]	100x.	$10^{-5} K_{hydr.}$
32	89.12	88.00	0.597	8.9
64	93.50	91.58	0.625	16.3
64	93.31	91.58	0.564	20.0
128	96.95	94.42	0.824	18.7
128	97.09	94.42	0.873	16.8
256	99.02	95.21	1.241	16.43
256	98.87	95.21	1.196	17.7

Mean, 16.4×10^5

For this compound, therefore, $k_{base} = 19.7 \times 10^{-9}$.

In Table XI. are given the results of the determinations of the velocity of decomposition of the hydrochloride in water at 25° (±0.01).

Table XI.

1. $V = 20$.

t.	cc.N/10 NaOH used.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH used.	$434.3 \times k_{salt}$.
0	12.50	....	195	9.42	0.630
10	12.28	(0.771)	315	7.93	0.627
40	11.75	0.672	1305	1.80	0.645
70	11.26	0.648			

Mean: $434.3\ k = 0.644$; $k = 0.00128$.

2. $V = 30$.

t.	cc.N/10 NaOH used.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH used.	$434.3 \times k_{salt}$.
0	8.33	...	330	5.07	0.654
10	8.20	(0.684)	1360	1.07	0.655
190	6.27	0.649			

Mean: $434.3\ k = 0.653$; $k = 0.00150$.

For the 1/20 molar solution, we have $k_{ion} = 0.00175$. For the 1/30 molar solution, $k_{ion} = 0.00172$.

---

[1] N/80 free base was used.

5. *The Hydrochloride of Methyl Imido-o-toluylate.*

Attempts were first made to prepare the ethyl ester by the usual method from the nitrile by the action of hydrogen chloride and alcohol, but with no more success than Pinner[1] had. The following three experiments were carried out:

1. Equal molecular weights of the nitrile, alcohol, and dry hydrogen chloride were used.
2. Equal molecular weights of the nitrile and acid, and ten molecules of alcohol.
3. A gram of the nitrile was dissolved in ten molecules of alcohol, and the mixture saturated with dry hydrochloric acid gas.

In none of the experiments was a trace of the imidoester formed.

A second attempt was made to prepare the ethyl ester by ethylating the silver salt of the acid amide. The amide was made by heating for several hours a mixture of *o*-tolyl nitrile and hydrogen peroxide,[2] and by heating a mixture of the nitrile and concentrated sulphuric acid. The latter method proved the better. The following method of converting the amide into the silver salt gave the best results: The amide was dissolved in hot dilute alcohol and the silver nitrate and sodium hydrate added simultaneously, drop by drop. In this way, a voluminous, white precipitate of the silver salt was obtained, which decomposed slightly on being washed with cold water. The analyses of the body gave the following results:

I. 0.1004 gram substance gave 0.0455 gram Ag.
II. 0.3099 gram substance gave 0.1401 gram Ag.

	Calculated for $C_8H_8ON.Ag$.	Found I.	Found II.
Ag	44.61	44.82	45.20

All attempts to alkylate this salt with ethyl iodide failed. In no case did the ethereal extract give a trace of the hydrochloride when dry hydrogen chloride was passed through it.

Methyl iodide was then tried. It was added to a mixture of the silver salt and a little ether, and the mixture allowed to stand from 24 to 48 hours. It was then extracted with ether, and when dry hydrogen chloride gas was passed through the extract, the hydrochloride of methyl imido-*p*-toluylate separated out in small, white flakes. A second treatment with methyl iodide gave a little more of the substance, but the total yield was small. The hydrochloride crystallizes in small, white flakes, and has a very agreeable cinnamonlike odor. On being heated rapidly it decomposes with effervescence and the resulting gas burns with a green flame. The solid residue (the amide) melts at 138°. If heated slowly, the salt decomposes without visible effervescence. Analyzed for chlorine, the salt gave the following results:[1]

---

[1] Pinner: Imidoaether, p. 63.

[2] Radzewski: Ber. d. chem. Ges., 18, 355 (1895).

0.149 gram substance required 8.07 cc. N/10 NaOH.

	Calculated for $C_9H_{12}NOCl$.	Found.
Cl	19.13	19.23

In Table XII. are given the data for the calculation of the hydrolysis constant of this compound at 25° (±0.01).

Table XII.

V.	M_v.	Λ_v.	$100x$.	$10^{-5} K_{hydr.}$
32	99.01	94.8	1.409	1.6
64	104.8	98.0	1.90	1.75
128	109.6	101.2	2.80	1.6
256	113.1	103.3	3.01	2.75
			Mean,	1.90×10^5

$k_{base} = 2.3 \times 10^{-9}$.

In Table XIII. will be found the results of the determinations of the velocity of decomposition of the hydrochloride in water at 25° (±0.01).

Table XIII.

1. $V = 32$.

t.	cc. N/10 NaOH used.	$434.3 \times k_{salt.}$
0	7.81	....
1001	2.55	0.486
1419	1.61	0.483

$k = 0.00111$ and $k_{ion} = 0.001276$.

---

[1] The titration was made with phenolphthalein by the method described by Miss Barnard (see a later paper).

6. *The Hydrochloride of Ethyl Imidophenylacetate.*

On account of the rapid decomposition of this salt in water, a double method of extrapolation was resorted to in order to find M_v and Λ_v at $t = 0$. An explanation of the method of extrapolation for the 1/32 molar solution will be given in the following table, XIV. The temperature of the experiments was 25° (±0.02):

Table XIV.

1.32 molar solution.

t	$10^6 \times K$.	Δ.	Δ5 min.	Δ_Δ.	$10^6 \times \kappa_0$.
0	....	...	(353)	..	(2816)
5	3169	125	312	29	...
7	3294	170	283	21	...
10	3464	105	262	74	...
12	3569	113	188		...
15	3682				...
			Mean,	41	

In Table XV. will be found the data for the determination of the hydrolysis constant at 25° (±0.01).

Table XV.

V.	M_v.	Λ_v[1].	$100x$.	$10^{-5} K_{hydr.}$
32	90.11	85.56	1.15	2.4
64	95.76	91.01	1.55	2.6
128	98.11	93.19	1.60	5.0
			Mean,	3.3

$$k_{base} = 4 \times 10^{-9}.$$

In the following table, XVI., are given the values of the determinations of the velocity of decomposition, referred to the concentration of the salt (equation 9) and also to the concentration of the free base (equation 10), for a 0.05 molar solution at 0° (±0.01).

---

[1] N/80 free base was used.

Table XVI.

t.	cc. N/10NaOH.	k_{base}.	434.3k_{salt}
20	10.52	....	....
50	8.80	0.6722	2.59
80	7.38	0.6380	2.57
110	6.26	0.5986	2.51
140	5.29	0.5718	2.40
185	4.25	0.5204	2.38
275	2.60	0.465	2.38

Mean: 434.3 k_{salt} = 2.47; k = 0.00569.

This gives k_{ion} = 0.00673.

The velocity constants for the decomposition of 0.05 molar solution of this salt at 0° (±0.01) in 0.05 and 0.15 molar solutions of hydrochloric acid were also determined. The results are given in Table XVII. Columns 2 and 5 gives the cc. sodium hydroxide used for 25 cc. of the salt solution, *corrected* for the alkali used to neutralize the excess of added acid.

Table XVII.

1. 0.05 molar acid.

t.	cc. N/10 NaOH.	434.3 × k_{salt}.	t.	cc. N/10 NaOH.	434.3 × k_{salt}.
0	12.50	....	130	5.71	2.32
10	10.85	....	160	4.86	2.32
40	9.22	2.36	190	4.14	2.33
70	7.80	2.39	291	2.41	2.33
100	6.68	2.34			

Mean: 434.3 k = 2.34; k = 0.00539.

2. 0.15 molar acid.

t.	cc. N/10 NaOH.	434.3 × k_{salt}.	t.	cc. N/10 NaOH.	434.3 × k_{salt}.
0	12.50	....	116	6.72	2.11
21	10.67	....	145	5.78	2.15
55	9.02	2.15	175	4.96	2.16
85	7.83	2.10	205	4.26	2.17

Mean: 434.3 k = 2.14; k = 0.00493.

In the following table the velocities are referred to the concentrations of the positive imidoester ion only (see Table IV.):

Table XVIII.

m_{acid}.	*Est salt.*	$100\alpha_{salt}$.	$434.3k_{salt}$.	$434.3\ k_{salt}/\alpha$.
0.00	0.05	84.6	2.47	2.92
0.05	0.106	80.0	2.34	2.93
0.15	0.24	69.0	2.14	3.10

This series shows clearly both the influence of the degree of dissociation of the imidoester salt and also the accelerating "effect" of the acid ions, as developed in Table IV. The series is too short for the determination of an accelerating constant.

7. *The Hydrochloride of Ethyl Imido-m-nitrobenzoate.*

In Table XIX. are given the results of the determinations of the velocity of decomposition constants for a 0.05 molar solution of the hydrochloride alone at 25° (±0.01), and of the 0.05 molar salt in 0.5 and 0.025 molar hydrochloric acid solutions. 25 cc. of the solution were used in each titration, corresponding to 25 cc. N/10 thiosulphate when $t = 0$.

Table XIX.

1. 0.05 molar salt alone.

t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.	t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.
62	4.25	12.4	120	1.19	11.0
120	1.15	11.2	60	4.75	12.0
60	4.73	12.1	120	1.10	11.1

Mean: $434.3\ k_{salt} = 11.67$; $k = 0.027$.

2. 0.05 molar salt in 0.025 molar hydrochloric acid.

t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.	t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.
60	5.08	11.1	60	5.50	11.0
120	1.59	10.0	120	1.37	10.5

Mean: $434.3\ k = 10.64$; $k = 0.0245$.

3. 0.05 molar salt in 0.5 molar hydrochloric acid solution.

t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.	t.	cc. N/10 thio-sulphate.	434.3 × k_{salt}.
60	6.39	9.89	60	6.26	10.02
120	1.76	9.60	120	1.78	9.54

Mean: $434.3\ k = 9.76$; $k = 0.0225$.

In Table XX. the columns have the same significance as in Table XVIII.

Table XX.

m_{acid}.	Est salt.	100α.	$434.3\ k_{salt}$.	$434.3\ k_{salt}/\alpha$.
0.0	0.05	84.6	11.67	13.80
0.025	0.08	82.2	10.64	12.9
0.5	0.80	48.0	9.76	20.3

The series shows the general effect discussed in full for ethyl imidobenzoate, and is too short for detailed analysis. A characteristic fact, however, is that the accelerating "salt effect" of 0.5 mole hydrochloric acid is practically the same in this case $\left(\frac{20.3 - 13.8}{13.8} = 0.47\right)$ as it was found above for ethyl imidobenzoate $\left(\frac{2.36 - 1.63}{1.63} = 0.45\right)$. If the "effect" is indeed due to the increase of the "active mass" of water, we should expect just such a result.[1] This is especially interesting in view of the great difference in the actual velocity constants.

The velocity of decomposition of the salt was also determined at 0° (±0.01) in 0.05 and 0.033 molar solutions.

Table XXI.

1. $V = 20$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
0	12.50	...	295	7.79	0.646
55	11.12	...	415	6.50	0.668
175	9.37	0.620	1375	1.66	0.626

Mean: $434.3\ k = 0.639$; $k = 0.00147$; $k_{ion} = 0.00174$.

2. $V = 33$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
114	6.83	...	304	5.16	0.641
179	6.18	0.668	1214	1.34	0.643
234	5.71	0.648			

Mean: $434.3\ k = 0.650$; $k = 0.00150$; and $k_{ion} = 0.00171$.

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[1] This has been investigated further in this laboratory.—J. S.

In Table XXI*a*. are found the data for the determinations of the hydrolysis constant of this salt at 25° (±0.01).

Table XXIa.

V.	M_v.	Λ_v[1].	$100\,x$.	$10^{-4}\,K_{hydrolysis}$.
32	94.1	88.13	1.925	8.2
64	100.35	92.8	2.792	7.98
128	107.5	95.4	3.957	7.8
256	112.4	96.9	5.064	9.5
			Mean,	8.4

$k_{base} = 1 \times 10^{-9}$.

8. *The Hydrochloride of Ethyl Imido-m-brombenzoate.*

In Table XXII. are given the results of the velocity determinations of 0.05 and 0.033 molar solutions of the hydrochloride at 0° (±0.01).

Table XXII.

1. $V = 20$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
85	11.32	...	1545	5.78	0.213
205	11.15	0.211	1820	5.12	0.209
325	10.52	0.211	2995	2.95	0.207
1325	6.50	0.209			

Mean: $434.3\,k = 0.210$; $k = 0.000483$.

2. $V = 30$.

t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.	t.	cc.N/10 NaOH.	$434.3 \times k_{salt}$.
80	8.03	...	1535	3.93	0.213
200	7.46	0.267	1812	3.41	0.215
320	6.98	0.254	2985	1.88	0.217
1320	4.32	0.217			

Mean: $434.3\,k = 0.231$; $k = 0.000532$.

k_{ion} for 0.05 molar solution = 0.000571.
k_{ion} for 0.033 molar solution = 0.000609.

9. *The Hydrochloride of Ethyl Imido-β-naphthoate.*

The data for the calculation of the velocity of decomposition constants of 0.033 molar solution of the hydrochloride at 25° (±0.01) are given in Table XXIII.

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[1] N/80 base was used.

Table XXIII.

t.	cc.N/10 NaOH.	434.3 × k_{salt}.	*t.*	cc.N/10 NaOH.	434.3 × k_{salt}.
21	7.93	1.018	201	5.24	1.001
51	7.43	0.970	231	4.91	0.993
82.5	6.92	0.976	261	4.58	0.995
111	6.51	0.965			

Mean: $434.3\ k = 0.988$; $k = 0.00251$.

In Table XXIV. will be found the data for the calculation of the hydrolysis constant at 25° (±0.01).

Table XXIV.

V.	M_v.	Λ_v^{I}.	$100x$.	$10^{-5} K_{hydr}$.
32	90.02	87.84	0.878	4.1
64	95.68	91.84	1.25	4.0
128	98.97	95.21	1.23	8.4
256	101.78	96.61	1.687	9.8
				Mean, 6.6

$$k_{base} = 7.92 \times 10^{-9}.$$

SUMMARY.

1. The nine imidoesters examined are decomposed by water in the presence of acids with a velocity proportionate to the concentration of the salt (positive ions) formed with the acid.

2. The results also contribute evidence that not all the salt present but only its positive ions are decomposed by water. This becomes apparent, not only from the results given in Table IV. (p. 598), taken in conjunction with the "salt effect" summarized in the next paragraph, but also from the following table, in which the velocities referred to the total salt concentrations are compared with the velocities referred to the total positive ion concentrations in all cases where determinations were made with varying concentrations.[2]

Table XXV.

Ester[3]	2.		3.		4.		7.		8.	
k_{salt}[4]	296_{20}	303_{30}	295_{20}	283_{10}	148_{20}	152_{30}	147_{20}	150_{30}	43_{20}	53_{30}
k_{ion}	350	346	349	350	175	174	174	171	57	61

[1] N/100 base was used.

[2] The experiments described here were intended (1899) to test conclusion (1), and they only incidentally contribute to the conclusion reached in (2). This point was investigated *rigorously* in Mr. Schlesinger's later work (1904–5) with more concentrated salt solutions, whose degree of ionization was *measured* (*loc. cit.*).

[3] The numbers in this line refer to the ester used, as numbered in the experimental part.

[4] The numbers used are 10^5 times the true constants. The subindices used give the volume containing a gram molecule of salt.

While the differences are not large, dilute solutions having been used, it is worthy of note that in every case the agreement for k_{ion} for the different solutions is better, and sometimes markedly so, than for k_{salt} (*e. g.*, for ester 3 where the difference in ionization is greatest).

3. The presence of an excess of hydrochloric acid has a twofold effect: it decreases the velocity of the reactions by reducing the degree of ionization of the imidoester salt, thus diminishing the "active mass" of the reacting substance, the positive ester ion; at the same time, an accelerating "salt effect" is decidedly shown, this effect, according to Euler, being probably due, in similar cases, to the increased ionization of the water, *i. e.*, the "active mass" of the second reacting substance is increased, as the other is decreased, by addition of the acid. The acceleration due to this effect was found to be practically the same (45 and 47 per cent) for the same excess of acid (0.5 mole acting on 0.05 molar salt) acting on the salts of two imidoesters whose velocities of decomposition stand in the ratio of about 10:1. This striking fact tends to confirm the view that the accelerating "salt effect" is, in fact, due, not to any primary action on the salt, but to an effect on the "active mass" of the water involved in the reaction.

4. Table XXVI. summarizes the data obtained in regard to any possible relation between the velocity constants (for 25°) of decomposition according to equation (1) and the hydrolysis constants of equation (2).

Table XXVI.

No.	Ester.	$10^5 k_{ion}$.	$10^{-5} K_{hydrolysis}$.
1.	Ethyl imidobenzoate	377	9.1
2.	Isobutyl imidobenzoate	350	10.4
3.	Isoamyl imidobenzoate	349	14.0
4.	Ethyl imido-*p*-toluylate	175	16.4
5.	Ethyl amino-*o*-toluylate	128	1.9
8.	Ethyl imido-2,6-nitrobenzoate	3200	0.8
9.	Ethyl imido-3-naphthoate	251	6.6

The numbers refer to the number given the esters in the experimental part.

Inspection of the table shows that with two exceptions the velocity constants decrease in the same order in which the strength of the imidoesters as bases (indicated by the rising values of $K_{hydrolysis}$) increases; one of the exceptions, ester No. 5, is the imidoester of *o*-tolunitrile. This nitrile, it will be recalled (p. 603), cannot be converted into an imidoester on account of the stereochemical interference of the methyl group in the ortho position.[1] As in the analogous case of the acid esters, as studied by V. Meyer,[2] the stereochemical interference also delays decomposition of the ester when once formed (from silver salts). We have in this exception, therefore, a further interesting case of parallelism between esters and imidoesters. The other exception is an ester of the naphthalene series. For the strictly comparable esters of the benzene series, we find, as a matter of fact, then, the velocity of decomposition is greatest, the weaker the base is; this points toward the interesting conclusion, based on the real reaction equation which we have established,

$$\mathrm{RC(:\overset{+}{N}H_2)OR + HOH = RCOOR + \overset{+}{N}H_4},$$

that the weaker the base in an analogous series, the less stable is its positive ion, and the more readily does it yield a positive ion (NH_4) of a more easily ionizable base.[3] Whether a widely applicable principle is involved in this, only very extended further investigations can show. My results show that it holds only for the more closely related members of a group,[4] as indicated by the exceptional position of the naphthimido ester, and particularly also by a comparison of the velocity constants (at 0°) for ethyl imidophenylacetate and ethyl imido-*m*-nitrobenzoate.

Table XXVII.

	Ester.	$10^5\ k_{ion}$.	$10^{-5}\ K_{hydrolysis}$.
6.	Ethyl imidophenylacetate	637	3.3
7.	Ethyl imido-*m*-nitrobenzoate	174	0.84

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[1] Remsen: This Journal, **21**, 281 (1899).

[2] *Loc. cit.*

[3] *Vide* Stieglitz: *Loc. cit.*

[4] A comparative study of the *heats of decomposition* of different groups will be carried out.—J. S.

It is worthy of note, however, that the imidoester of phenylacetic acid, compared with its isomer, *p*-tolylimidoester, and with the closely related esters of benzoic acid, takes its right position in the series.[1]

In conclusion, I desire to express my thanks to Dr. Stieglitz for his help and encouragement in the prosecution of this work.

THE TERPENES OBTAINED FROM INDIVIDUAL SAMPLES OF THE RESIN, MANILA ELEMI.

By A. M. Clover.

During the course of some work with elemi resin, in Manila, it was observed that the oils distilled from different samples of the product, obtained from several dealers, were not the same in composition. While our present knowledge of terpenes does not enable us to determine, even qualitatively, the composition of a mixture of different substances of this class, still certain variations were easily recognized. The low-boiling fractions, which consisted, in all cases, of the simple terpenes only, differed widely in their optical rotation and decidedly, though to a lesser extent, in their boiling point. Phellandrene, limonene and dipentene could be detected in certain cases, and in others could not. The high-boiling portions of the distillate, which were readily separated from the low-boiling terpene fractions, also varied greatly in refractive power and specific gravity. Definite knowledge concerning the origin of the resin was lacking and it was suspected that possibly the product was not derived from a single species of tree. It also seemed possible that changes might have taken place in the resin as a result of long standing.

Later two small, fresh samples, said to have been gathered from single trees, were examined. The low-boiling oil isolated from one of these was found to be dextrophellandrene, and that isolated from the other, dextrolimonene, and both were pure so far as the detection of any other terpene was concerned. From botanical material which had been collected from each of the trees, the two were judged to be of the same species.

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[1] A comparative study of aliphatic and aromatic acid derivatives and especially of aliphatic acids, RCH_2COOH, $R_2CHCOOH$, R_3COOH, has been planned on the basis of the new lines opened up, especially with the view of obtaining physico-chemical evidence on the formation of $CH_2=CO$ and analogous derivatives as intermediate products. I hope the physico-chemical investigation of this problem will, for a little while yet, be left to us.—J. Stieglitz.

Most plant products consist of the aggregate obtained from many individuals and I know of no case where chemical differences in the substances produced by individual members of a species have been recognized or suspected. In order to obtain more accurate data upon the subject, I made a trip into the Province of Tayabas, P. I., and in different places collected several samples of the *pili* (Tagalog) resin, from trees differing in size and sex. At the same time leaves of each tree, and also the fruit of those trees bearing it, were preserved. All of the trees appeared to be alike and, from the botanical material, they were all assigned to the species *Canarium luzonicum* by Mr. E. D. Merrill, Botanist to the Bureau of Science of the Philippine Government.

The samples were obtained as fresh as possible, considering the fact that the resin must have remained on the trees for a month or so in order to allow of the production of a fairly large quantity. The different samples were well wrapped in palm leaves and were all worked up within four months after being gathered. The results developed by their examination not only confirmed what had been suspected in regard to variation, but showed that *in the majority of cases, in each individual sample a definite terpene of the limonene series occurred in a pure condition.*

In order to obtain larger quantities of these pure terpenes and to extend the results already obtained, and also with the hope of isolating one or more of the unknown terpenes of this class, another collecting trip was made and 14 more samples were gathered, just as in the previous case. All of these latter were worked up within four months after they were collected. *As a result of the complete examination of 21 samples, it has been possible to isolate the terpenes dextrolimonene, dextrophellandrene, terpinene and terpinolene in pure condition and* *to study the behavior of these substances; to render certain the presence of an unknown terpene in several products; to establish regularities in the occurrence of certain mixtures where the terpene product is not homogeneous; to isolate in pure condition, from single samples, two of the constituents of the high-boiling portion of the oil; and to determine the composition of the mixture which constitutes the high-boiling oil obtained from most samples.* The high-boiling oil which occurs in elemi and can be most conveniently and completely removed by distillation *in vacuo* was shown to be a mixture of at least three substances. Here, also, a great variation has been found in the different samples, but no connection appears to exist between the terpene and the corresponding high-boiling oil. No connection can be traced between the age or sex of the tree and the constituents of the oil.

General Data Concerning the Resin and Oil.

From a number of tropical countries products known as elemi find their way into European markets. The species from which most of these varieties are derived is unknown, but there is little doubt that they are all to be referred to the general order of *Burseraceae*. A. Tschirch and J. Cremer[1] have recently arrived at the definite conclusion that Manila elemi is derived from *Canarium commune* L. Their conclusion is the result of an examination of samples of Manila elemi and resin obtained by one of the authors in India from the species *Canarium commune*, and is based upon a comparison of the general properties of the two products as well as of the crystalline substances isolated therefrom. So far as their work went they were unable to note any differences between the two products.

The tree *Canarium luzonicum* is quite widely distributed in the Philippine Islands and is known by the Tagalogs as *pili*. There are two closely related species designated as *pili*. *Canarium luzonicum* bears a small nut, while the other, which has been identified by Mr. Merrill as *Canarium pachyphyllum*, bears a much larger nut, produces resin in only very

[1] Arch. d. Phar., **240**, 313 (1902).

small amounts, and is never used by the natives as a source of the latter.

In the Philippines the resin is commonly known by the Spanish term *brea*, which is applied by the natives indiscriminately to all similar products. As ordinarily gathered for commerce, the resin is soft, sticky and opaque and has a slightly yellow color and an agreeable odor. If not frequently removed from the tree it hardens and loses a portion of its oil through volatilization and oxidation. The fresh resin contains nearly five per cent of water and about thirty per cent of volatile oil. The latter is composed of about equal parts of a low-boiling portion, consisting of terpenes, and of a high-boiling portion, containing oxygen compounds.

Elemi oil, usually obtained by steam distillation of the resin, has long been known to chemists. Gildemeister and Hoffmann[1] state that at present the commercial product is prepared from Manila elemi exclusively, although in most cases where the oil has been used in chemical investigations there seems to be much doubt as to its origin. The oil was first studied by Stenhouse,[2] and some years later Deville[3] obtained from it dipentene hydrochloride. Wallach[4] detected phellandrene and dipentene in the oil and has used it as a source of these substances. He also noted the presence of high-boiling oxygen compounds. Schimmel and Co., in their semiannual report of October, 1896, publish some observations concerning the high-boiling portion of the oil. Tschirsch and Cremer[5] have distilled Manila elemi, as well as other varieties, with steam and obtained oils, but the very meagre data which they give do not enable one to decide what differences, if any, exist in the oils.

Distillation of Resin and Purification of Oils.

Owing to the fact that the resin becomes more and more viscous as the volatile oil is removed, the distillation with steam is slow and unsatisfactory. It was desired to remove all the oil possible and at as low a temperature as possible, in order to prevent any change taking place in it. For this purpose it was found much better to distil in a vacuum. It was also found that the high-boiling oil could be almost completely removed from the resin at a pressure varying from 8 to 15 mm., with practically no decomposition of the latter. To introduce the resin into the distilling flask, it was first placed in a beaker and immersed in an oil bath which was kept at a temperature of from 100° to 125°, depending on the ease with which the resin became fluid. The latter was then poured into the flask and the terpene oil distilled over *in vacuo*, the pressure being gradually decreased to 10 or 15 mm. as the water in the resin passed over; the oil bath was kept between 125° and 150°. The distillation was always made as quickly as possible and in no case was purified terpene oil derived from a product which had been heated higher than 150°. Frequently a second distillate was then taken by heating to 200°, at which temperature practically all of the terpene but only a portion of the high-boiling oil may be removed. If the resin is quite fresh, most of the heavy oil will have passed over before the oil bath reaches 230°, but with an old product it is difficult to maintain a high vacuum, so that the oil bath must be heated to 250°. At this temperature, with fresh material, there is very little, if any, decomposition of the resin, but with old samples it is possible to remove only a small portion of the high-boiling oil because of the increasing difficulty of maintaining a vacuum as the temperature is raised beyond 200°. In several instances, the purified, high-boiling oils derived from fresh resin at 200° were found to be identical with those obtained from the same samples when, in some cases, the temperature was raised as high as 250°; so that it is quite certain that no changes have been brought about in these oils by the high temperature.

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[1] Die aetherischen Oele, Berlin (1899).

[2] Ann. Chem. (Liebig), **35**, 304 (1840).

[3] *Ibid.*, **71**, 352 (1849).

[4] *Ibid.*, **246**, 233 (1888); **252**, 102 (1889).

[5] *Loc. cit.*

Sample I. was collected in July near Unisan, Tayabas Province, Luzon, from a relatively young tree about 40 feet in height, having a diameter of about 2 feet near the base. There was no fruit on the tree and its owner said it never had borne any. The resin was drier than most of the samples and yielded only about seventeen per cent of oil.

The first distillate (I,A) was taken at 140°, the second up to 210° (I,B), and the third up to 250° (I,C).

I,A was redistilled twice at 54 mm.; it passed over completely, the second time, from 93° to 94° (I,A, purified). Its optical rotation was $\alpha_D^{30} = +99°.6$.[1] The oil gave no test for phellandrene. It was found that on the addition of even only 1 per cent of an oil known to be nearly pure phellandrene, it responded plainly to the test when the solution was kept very cold. In the proportion of 1 to 200 no test could be obtained. With bromine in acetic acid, limonone tetrabromide was obtained. This melted at 104°–105° after the second crystallization from alcohol. The oil, treated with hydrochloric acid gas in glacial acetic acid, gave a good yield of dipentene dihydrochloride, which, after recrystallization from alcohol, melted at 49°–50°. I,A, purified, gave a granular nitrosylchloride when treated according to the method of Wallach. The odor of the oil was plainly that of commercial carvene. When heated with metallic sodium it was very little affected, and after having been distilled from the metal it was found to pass over completely at ordinary pressure from 176°.5 to 177°.5. It appears to be pure dextrolimonene.

Sample II. was collected near Atimonan, Tayabas, from a tree having a diameter of about 3 feet near the base and laden with unripe nuts. The sample was softer than the previous one and yielded 25 per cent of oil.

The first distillate was taken at 125° (II,A), the second at 210° (II,B), and the third at 250° (II,C).

II,A was decanted from a small amount of water which collected with it. It was distilled twice at 36.5 mm., passing over the second time almost completely between 82°.5 and 83.°5; three-fourths of it distilled at almost a constant temperature, or at most within 0°.25 (II,A, purified). $\alpha_D^{30} = +100°$. The product, so far as could be determined, was identical with that obtained from *Sample I.*

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[1] This form of expression will be used to express the rotation in a ten cm. tube at the temperature indicated.

Sample III., which was quite soft, was obtained from a young tree, smaller than that from which *Sample I.* was taken, and standing very close to the latter tree. It was first distilled at 125° for the terpene oil (III,A) and then at 210° (III,B). In all, 186 grams of distillate were obtained from 900 grams of resin. A further distillation was not made.

III,A, on the third distillation at 47 mm., passed over completely from 89° to 90°. $\alpha_D^{30} = +100°.7$. The purified oil had the same odor, boiling point and optical rotation as the two previous terpene products.

Sample IV. was collected near Unisan, Tayabas, from a good-sized tree, nearly 3 feet in diameter near the base. The tree, which bore no fruit, contained 8 to 10 pounds of soft resin.

One thousand and eighty grams of the sample were distilled, first at 125° (IV,A), then at 210° (IV,B) and finally at 250° (IV,C). The total amount of terpene oil obtained from this sample was 152 grams, or 14 per cent, and of high-boiling oil, 145 grams, or 13.4 per cent.

IV,A was redistilled twice at 65.5 mm., and on the second distillation it passed over completely from 95°.5 to 97°.5 (IV,A, purified). It was almost optically inactive ($\alpha_D^{30} = +4°$). It gave no test for phellandrene. In a check experiment in which a very small proportion of phellandrene was added to the oil, this was easily detected. No crystalline hydrochloride could be obtained on treatment with hydrochloric acid gas in cold, glacial acetic acid, nor could a crystalline bromide be separated on saturation with bromine, either in acetic acid or in a mixture of amyl alcohol and ether. No solid nitrosylchloride could be obtained. A good quantity of terpinene nitrite was obtained by using the method recommended by Wallach, the crystals appearing in a short time. When recrystallized from alcohol, this substance melted at 155°, softening a little below that temperature. The oil was distilled from metallic sodium, after which it boiled completely from 174° to 176°. It stood nearly a year in a partially filled glass-stoppered bottle; it was then redistilled with steam, separated from water, and dried over solid caustic potash. Boiling point, 174° to 175°.5. Sp. gr. $\frac{30°}{4}$ = 0.8358. $\alpha_D^{30°} = +4°.3$. $n_D^{30°} = 1.4756$. The product still gave a good yield of terpinene nitrite and in all other respects it behaved as it had one year previously. It appears to be almost pure terpinene. In physical properties it does not differ much from limonene except in refractive power (see page 631). Terpinene has been detected in only two of the natural essential oils. It has also been shown to be present in several products resulting from chemical operations in the laboratory. In general, those fractions boiling at about 180° appear to have given the best yield of the nitrite.

IV,B was distilled under reduced pressure and the low-boiling portion was refractioned. On the third distillation it passed over completely, within a range of 2°.5 or 3°, and was evidently not so pure a product as that obtained from IV,A, although it gave a good yield of terpinene nitrite. It appears that in this case, as well as with the samples containing phellandrene, there is some alteration in the terpene when it is removed from the resin at higher temperatures.

Sample V., which was moderately soft, was obtained from a tree standing close to that from which *Sample II.* was taken. The tree was laden with unripe nuts.

The resin was distilled, first at 125° (V,A), then at 210° (V,B) and finally at 250° (V,C). The total terpene oil amounted to 9.7 per cent and the high-boiling oil to 15.8 per cent.

V,A, on the second distillation at 43.5 mm., passed over almost completely from 82°.7 to 84° (V,A, purified). Its odor was very pleasant and markedly different from that of any of the terpene products previously obtained. $\alpha_D^{30°} = +122°.6$. It yielded a very heavy precipitate of phellandrene nitrite. Neither a solid bromide nor a nitrosylchloride could be obtained by the methods ordinarily used. The product appears to be almost pure phellandrene. Its boiling point is 3° or 4° below that of the limonene oils and about 2° below that of the terpinene oil. On standing in a partly filled glass-stoppered bottle, a small amount of good-sized, colorless, prismatic crystals appeared about the walls of the bottle.

Sample VI. was obtained near Atimonan, Tayabas. The tree was an unusually large one, being 5 or 6 feet in diameter near the base. A large quantity of soft resin had accumulated from a number of cuts. The tree bore no nuts and a native familiar with it declared that it had never produced any.

The first distillate (VI,A) was taken at 125°, and the second up to 225° (VI,B). The two amounted to 25 per cent of the resin.

VI,A passed over completely from 93° to 94° at 55 mm. on the second distillation (VI,A, purified). It had the same characteristic odor as the product obtained from the previous samples of limonene which had been isolated and its boiling point is also the same. $\alpha_D^{30} = +99^\circ.9$. In rotation, its agreement is seen to be remarkable. Pure limonene tetrabromide was obtained from it and it was also tested thoroughly, just as the oils from *Samples I.* and *II.*, and it showed exactly the same behavior. By comparing the terpene oils obtained from *Samples I.*, *II.*, *III.* and *VI.*, especially as to rotation, it appears that when dextrolimonene occurs in the resin from a single tree it is present in pure condition.

Sample VII. was obtained near Atimonan, Tayabas, from a tree about 2 feet in diameter, laden with unripe nuts. The sample was a little hardened, but only on the outside.

Nine hundred and sixty grams were distilled, first at 125°, yielding 57 grams of distillate, excluding 3 or 4 grams of water (VII,A). A second portion, 128 grams, was taken to 210° (VII,B), and a third, 73 grams, to 250° (VII,C). The total distillate, 258 grams, consisted of about equal parts of terpene oil and heavy oil, or 13.4 per cent of each.

VII,A, on the third distillation at 39 mm., passed over from 76°.5 to 79° (VII,A, purified). $\alpha_D^{30} = +114^\circ.7$. The product had the odor of phellandrene, but it also possessed another peculiar odor not noticeable in any of the other terpene products. Its initial boiling point is a few degress lower than that of the sample of presumably pure phellandrene already isolated. The oil gave a precipitate of phellandrene nitrite in good quantity, but many attempts to isolate any other crystalline derivative from it by any of the methods ordinarily employed were unsuccessful. The product was then distilled at ordinary pressure and two fractions of equal size were taken—(1) from 167°.5 to 169°; (2) from 169° to 172°. The first fraction showed a rotation of +110°.1 and the second +113°.1. The first fraction was tested in a number of ways in the hope of isolating a crystalline substance other than phellandrene nitrite, but with negative results. On again distilling, its initial boiling point was lowered only about 0°.5. Both fractions deposited crystals on standing.

The work with the following samples was carried out in essentially the same manner as that already detailed. It was found that it was not necessary to use great precaution as to temperature in removing limonene from the resin; therefore, when a sample was found to contain dextrolimonene, the terpene was removed as completely as possible by heating the resin to 150° or 160°. Phellandrene suffers a considerable change at a temperature near its boiling point, and it was thought that terpinene would likewise suffer alteration at a higher temperature, especially when it was in contact with the resin. However, it was desirable to remove all of the terpene possible, so that the purified product could be used for further work. In those samples not containing dextrolimonene, the distillation was carried as far as possible at 125° and then the oil bath was heated gradually to 150° and the distillation made as quickly as it could be done. The entire distillate was taken in only two portions, the high-boiling part being seldom taken beyond a temperature of 235°. The products will be designated as A, first distillate, and B, second distillate. In order to obtain the correct data for the physical properties of the terpene oils, they were, unless otherwise stated, first shaken with a dilute solution of potassium hydroxide which freed them from an unpleasant odor often noticed, and then distilled twice *in vacuo*, allowed to stand overnight with solid potassium hydroxide, and then carefully redistilled, the first 2 or 3 cc. of the distillate being discarded. In a few samples, the high-boiling oil was disregarded entirely. The following samples were all obtained within a radius of a mile or two near the town of Gumaca, Tayabas, during the month of June.

Sample VIII. was taken from a tree a little over 2 feet in diameter. The tree bore no fruit. The resin had evidently collected for some time, there being a large amount of it, yellowish and somewhat incrusted, on the tree. The purified terpene oil boiled completely from 95°.3 to 96°.5, at a pressure of 60.5 mm., and at ordinary pressure from 176° to 176.°7. $\alpha_D^{30} = +100°.8$. It is evidently pure limonene.

Sample IX. was obtained from a tree, laden with nuts, of about the same size as that from which *Sample VIII.* was taken and standing close to the latter tree. The sample was a large one and somewhat dried out. The purified terpene oil boiled from 176°.5 to 177°.5. $\alpha_D^{30} = +100°.3$. It is evidently pure dextrolimonene, but the boiling point is slightly higher than that of the last sample.

Sample X. was taken from a medium-sized tree bearing fruit. The resin was fresh and soft. The terpene oil, after the usual purification, distilled completely from 89°.5 to 94°.5 at 65 mm., so that, therefore, the distillation began about 5° below the boiling point of phellandrene. $\alpha_D^{30} = +69°.3$. It gave a heavy precipitate of phellandrene nitrite. It was redistilled at ordinary pressure and the distillate divided into two equal portions: (1) 166°.5 to 168°.5; (2) 168°.5 to 171°.5. The first fraction showed sp. gr. $\frac{30}{4} = 0.8356$; $\alpha_D^{30} = +70°.4$; $n_D^{30} = 1.4663$; while the second gave sp. gr. $\frac{30}{4} = 0.8374$; $\alpha_D^{30} = +64°.6$; $n_D^{30} = 1.4680$. The first fraction was redistilled and there was very little lowering of the initial boiling point. The phellandrene nitrite obtained from the oil was recrystallized twice from hot acetic ester and it then melted at 114° to 115°. In its odor and boiling point this oil is very much like that obtained from *Sample VII.*; however, it seems to contain much more of the lower-boiling terpene. It appears from the data just given that this terpene has a considerably lower refractive power and specific gravity than phellandrene. As with the oil of *Sample VII.*, it was not found possible to obtain any solid derivative except phellandrene nitrite.

Sample XI. was small in amount, and to obtain enough terpene oil to work with, the latter was completely removed at a temperature of 200°. The oil was not purified *in vacuo* but was redistilled twice at ordinary pressure, passing over the second time mostly from 173° to 178°; $\alpha_D^{30} = -50°.7$. This is the only case in which a levorotatory oil has been obtained from a sample of elemi. The oil gave a precipitate of phellandrene nitrite, but the yield was not large. In cold, glacial acetic acid a tetrabromide was separated, but a much better yield was obtained in amyl alcohol and ether. When recrystallized twice from alcohol, it showed a melting point of 104° to 105°. The tetrabromide of levolimonene in chloroform at 9° and at a concentration of 12.85 per cent gives $[\alpha]_D = -73.45$, as determined by Wallach and Conrady.[1] The amount of pure bromide at hand was not large enough for an accurate estimation, but it was found to be levorotatory and to about the degree just mentioned. A small portion of it was carefully weighed out and mixed with exactly the same amount of pure dextrolimonene tetrabromide. The mixture was dissolved in a small amount of acetic ester, and alcohol was then added. On cooling, pure dipentene tetrabromide, melting at 124°, crystallized out. The oil, therefore, contains levolimonene and phellandrene, the latter being probably dextrorotatory. That the levolimonene was not formed by the action of heat upon the phellandrene will be seen from experiments given under phellandrene.

Sample XII. was taken from a medium-sized tree which bore no fruit. The resin was quite soft. The purified terpene oil obtained from this sample showed a boiling point of 176° to 176°.7 at ordinary pressure. $\alpha_D^{30} = +100°.3$. It is evidently pure dextrolimonene.

Sample XIII. was a large accumulation, somewhat incrusted, taken from a medium-sized tree with no fruit. The purified terpene oil was found to be pure dextrolimonene. Boiling point, 176°.5 to 177°.5; $\alpha_D^{30} = +100°.1$.

Sample XIV. was taken from a medium-sized tree bearing fruit. The resin was moderately soft. The purified terpene oil boiled from 91°.5 to 93° at 60 mm. Sp. gr. $\frac{30}{4}$ = 0.8322; $\alpha_D^{30} = +105°.1$; $n_D^{30} = 1.4694$. The oil gave a heavy precipitate of phellandrene nitrite. To judge from the boiling point, the oil appears to be nearly pure phellandrene, although the rotation is considerably lower than that of the phellandrene from *Sample V.*

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[1] Ann. Chem. (Liebig), **252**, 145 (1889).

Sample XV. was obtained from a very large tree, bearing no fruit. It was quite soft. The purified terpene oil boiled from 88° to 91° at 60 mm. Sp. gr. $^{30}_{4}$ = 0.8336; α^{30}_{D} = +112°.7; n^{30}_{D} = 1.4678. The initial boiling point was a little below that of phellandrene and the product was evidently a mixture. It gave a heavy precipitate of phellandrene nitrite. The oil redistilled at ordinary pressure from 169°.3 to 172°. The distillate was divided into two fractions, which showed practically the same rotation, a trifle lower than the original. No other crystalline derivative could be obtained from the oil. The odor is at once suggestive of the oils from *Samples VII.* and *X.*, which this oil resembles in most respects. During the purification, crystals were noted in the small residue contained in the distilling flask. Crystals also separated from the heavy oil which had been redistilled once and allowed to stand.

Sample XVI. was obtained from a good-sized tree about 3.5 feet in diameter near the base and bearing no fruit. The resin was fresh and soft. The purified terpene oil distilled completely from 89° to 90°.8 at 56.5 mm., most of it going over at almost a constant temperature. α^{30}_{D} = +129°.8; in a 5 cm. tube the rotation was just one-half as great. The oil had the characteristic odor of phellandrene and gave a heavy precipitate of the nitrite. A portion distilled completely at ordinary pressure from 172° to 173°.5. The product has the highest rotation of any sample of phellandrene obtained.

Sample XVII.—The purified terpene oil distilled almost completely from 86° to 87°.5 at 48.5 mm., a little higher, therefore, than the temperature at which phellandrene should distil. It contained much phellandrene but the rotation, as well as the boiling point, indicated that some other substance was present. α^{30}_{D} = +73°.5; n^{30}_{D} = 1.4693. A portion of it distilled from 173° to 174°.5 at ordinary pressure. No crystalline bromide could be obtained in acetic acid, nor in ether and amyl alcohol. No limonene could be detected by tests with ethyl nitrite in acetic acid or in ligroin. In preparing phellandrene nitrite, no crystals of terpinene nitrite appeared in the mother liquor on standing. The crude phellandrene nitrite was dissolved in a small amount of chloroform, filtered and precipitated with ether. It then melted at 114° to 117°. On recrystallizing from acetic ester without warming, it melted at 119°.5 to 121°. On again recrystallizing it melted at 120° to 121°. The crude nitrite obtained constituted about 50 per cent of the weight of the original oil. The rotation of the nitrite melting at 119°.5 to 121° was approximately that found by Wallach for pure α-phellandrene α-nitrite obtained from several sources, so that it appears that the low rotation of this sample of phellandrene and the variation observed in the rotation of the other samples obtained are not to be explained by assuming the presence of varying amounts of levophellandrene. It will be brought out later that the second substance in this oil is levolimonene.

Sample XVIII.—The purified terpene oil distilled completely from 88°.7 to 90°.4 at 54.5 mm. pressure. It was found to be phellandrene and, judging from the boiling point, was almost, if not quite, pure. The rotation, however, is somewhat lower than that of some of the phellandrene oils ($\alpha_D^{30°} = +113°.5$). After standing for two months the sample contained a small quantity of the familiar crystals.

Sample XIX. gave a purified terpene oil boiling from 90° to 91° at 50 mm. pressure. $\alpha_D^{30°} = +98°$; $n_D^{30°} = 1.4680$. It is evidently practically pure limonene, although the rotation is a little lower than usual. It was found impossible to isolate from the high-boiling oil of this sample any considerable portion which would show a narrow range in boiling point.

Sample XX.—The purified terpene oil from this sample distilled completely from 81.7° to 83° at 35.5 mm. $\alpha_D^{30°} = +97°$. The substance appeared to be practically pure limonene, although the rotation is lower than that of any other sample isolated. It gave no test for phellandrene.

Sample XXI. proved to be especially interesting. It was small in amount and was a fresh, soft resin when collected, although nearly four months elapsed before it was distilled. The terpene oil passed over on the second distillation almost completely within 1°, the boiling point lying between that of phellandrene and limonene. Its rotation was +4°. Because of its rotation and boiling point, it was at first supposed to be terpinene, but no test for terpinene could be obtained. The oil contained no phellandrene, according to notes made at the time it was distilled. There can be no doubt on this point, as the phellandrene nitrite would certainly have been noted in the test for terpinene, the tests always being made in essentially the same manner. On long standing, even after having been inoculated with a crystal of terpinene nitrite, no separation of this substance occurred. On the same day that the test for terpinene was made and when it was found that the terpinene nitrite was not being formed, the oil was treated with bromine in cold acetic acid and a crystalline bromide obtained. This was recrystallized from acetic ester. The crystals did not appear to be those of dipentene tetrabromide, as they melted at about 117°, with darkening and effervescence. The substance was recrystallized from alcohol, in which it appeared to be more soluble than dipentene tetrabromide. The crystals were lustrous plates and melted at 116°, with darkening and effervescence. It was noted at the time that these crystals were entirely different from those of dipentene tetrabromide, with which I was very familiar and which I rather expected to obtain when the test was made. The substance was certainly the tetrabromide of terpinolene, discovered by Wallach[1] in the product formed by the action of sulphuric acid upon American turpentine oil. He also obtained it from the oils resulting from the action of sulphuric acid upon terpine hydrate, terpineol and cineol. He gives 185° to 190° as the boiling point of the fraction yielding the bromide in the first case noted. Baeyer[2] also studied the substance and found that the bromide was best prepared from the oil which resulted from the action of a boiling solution of oxalic acid upon terpineol. By reducing the tetrabromide with zinc dust in cold acetic acid, Baeyer obtained a product which boiled from 183° to 185° and which gave a good yield of the tetrabromide. He found the terpinolene to be rapidly changed by the action of heat.

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[1] Ann. Chem. (Liebig), **230**, 262 (1885); **239**, 23 (1887).

[2] Ber. d. chem. Ges., **27**, 447 (1894).

The oil from the sample, as described above, was, as usual, shaken out with a dilute solution of caustic potash and then dried over solid caustic potash. It was redistilled on the next day, and at 37 mm. its boiling point was practically constant, 80° to 81°. The physical constants of the oil were now as follows: Sp. gr. $\frac{30^\circ}{4}$ = 0.8360; $\alpha_D^{30^\circ}$ = +1°.7; $n_D^{30^\circ}$ = 1.4701; boiling point, 173°.5 to 175°.

Up to this time only one day had elapsed since the removal of the oil from the resin. The alteration in its rotation between the second and third distillations was thought to be unusual and, with the idea of accelerating any change which was possibly taking place in the oil, a portion of it was heated for 3 hours in a tightly-stoppered distilling bulb, immersed in an oil bath at 200°. The product was then distilled. The range in boiling point appeared to be greater than before heating. The amount of polymerization was very small. *The distillate showed a rotation of —7°.5*, and was found to give a precipitate of *phellandrene* nitrite, although the amount obtained was not large. After the usual treatment of the crude product, namely, dissolving it in chloroform and precipitating with ether, it was recrystallized from acetic ester without warming and found to melt at 119° to 120°. The quantity was small, but a reading made in an approximately 1 per cent acetic ester solution showed it to be decidedly levorotatory.

Four or five days later an attempt was made to prepare more of the terpinolene tetrabromide from the purified oil. The tetrabromide obtained in acetic acid was recrystallized from acetic ester and now melted at about 120°. It appeared more like dipentene tetrabromide than like the derivative of terpinolene, and on recrystallization melted at 125°. The experiment was carefully repeated twice; the bromine, dissolved in an equal volume of glacial acetic acid and well cooled, was carefully added to an equally well cooled solution of the oil in 1.5 volumes of glacial acetic acid. The crude bromide, when recrystallized from acetic ester, melted from 118° to 120° with darkening, but in appearance and solubility it resembled dipentene tetrabromide. On recrystallizing again, it melted at 123° to 124°. The purified bromide was unquestionably that of dipentene, although the crude product appears to have been a mixture, for after the first recrystallization it was still impure.

At this point it was found that the purified oil gave a decided test for phellandrene. The rotation of the oil was also found to have changed from +1°.7 to —1°.6. *After standing for five or six days longer, the oil gave a rotation of —9°.8 and one month after this, of —34°.5, thus demonstrating that a rapid change was taking place spontaneously.* Three weeks later, the oil, which had stood in a cork-stoppered, partly filled flask, was distilled with steam. A small proportion of viscous, nonvolatile matter remained, probably the result of oxidation of the oil on standing. The distillate was separated from water, and without further drying gave $\alpha_D^{30} = -38°$. Judging from this value, in comparison with that obtained three weeks previously, it was evident that the change taking place had about reached completion. In amyl alcohol and ether the oil now yielded a very good quantity of a crystalline bromide which was recrystallized from a mixture of acetic ester and alcohol. The crystals melted at 122° to 124°. 0.24 gram of the substance dissolved in about 8 cc. of acetic ester and placed in a 10 cm. tube showed no appreciable rotation, so that the product apparently contained very little, if any, limonene tetrabromide. Certainly, the rotation of the oil cannot be accounted for by the presence of levolimonene. A good quantity of the bromide was also obtained in acetic acid. After crystallizing once from a mixture of acetic ester and alcohol, it melted at 120° to 123°; on recrystallizing from acetic ester its melting point was 125°. The product melting at 120° to 123° remained perfectly colorless on fusion, thus differing markedly from that obtained from the oil after four or five days' standing. An attempt was now made to prepare phellandrene nitrite again from the oil and to determine its rotation. Although the presence of phellandrene in the oil was readily shown, it was found impossible to isolate the nitrite in the presence of so much dipentene, the final product being a small amount of viscous matter adhering to the sides of the flask. This result is, of course, quite different from that obtained two months previously.

There appears to be no doubt that the oil, when first isolated, was nearly pure terpinolene; that this terpinolene changed completely, on standing, into dipentene, a small amount of dextrophellandrene and an unknown levorotatory terpene. The boiling point of this terpinolene is considerably lower than that obtained by Baeyer for the product formed on reducing the tetrabromide. The present case is the only one in which the presence of terpinolene has ever been noted in a natural product.

Limonene.

Limonene occurs generally in the dextrorotatory form as the chief component of a number of the most important essential oils of commerce. From some of these it has been obtained in a fair degree of purity by fractional distillation, but the physical properties of the substance, as given in the literature, vary somewhat, depending upon the degree of purity with which it is possible to isolate it from the other constituents of those oils by the process mentioned. From caraway oil, Schimmel & Co.[1] have isolated dextrolimonene, which showed a rotation of $[\alpha]_D = +123°.6$, while Kremers[2] obtained $[\alpha]_D^{20} = +120°.46$ for the carefully fractionated portion of commercial carvene boiling at 174°.5 to 175°, and presumably from the same source. For the levolimonene of pine-needle oil, Wallach found $[\alpha]_D = —106°$. Godlewsky and Robhanowitsch,[3] for the purpose of obtaining accurate data as to its physical constants, prepared what appears to be almost, if not quite, pure limonene by reduction of the pure tetrabromide. Their product, which is described as boiling at constant temperature, showed: sp. gr. = 0.8425; $[\alpha]^{20}_{\mathrm{D}} = +125^\circ.6$; boiling point, 177°.5 at 759 mm. Considering the small variation which I have found in the optical activity of the many constant-boiling samples of dextro-limonene obtained from different samples of elemi, this property appears to serve well as a check upon the purity of the limonene.

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[1] Gildemeister und Hoffmann: Die aetherischen Oele, 1899, p. 172.

[2] THIS JOURNAL, 17, 694 (1895).

[3] Centrabl., 1899, I., 1241.

The following table of physical constants for dextrolimonene is taken from some of the samples which have a rotation close to the average:

Purified product.	Boiling point, complete.	α^{30}_{D} +	n^{30}_{D}	Sp. gr. $^{30}_{4}$	Boiling point at reduced pressure.	mm.
VIII,A	176.0–176.7	100.8	1.4679	0.8353	95.3–96.5,	60.5
XII,A	176.0–176.7	100.3	1.4682	0.8350		
XIII,A	176.5–177.5	100.1	1.4683	0.8364		
IX,A	176.5–177.5	100.3	1.4680	0.8371[1]		
VI,A	176.0–176.7	99.9	....	....	93–94	55
II,A	176.0–177.0	100.0	....	....	82.5–83.5,	36.5

Product VIII,A, purified, showed: $n^{25}_{\mathrm{D}} = 1.4705$ and $n^{20}_{\mathrm{D}} = 1.4728$. An average difference of 0.0071 was found between specific gravity $\left(^{30^\circ}_{4}\right)$ and specific gravity $\left(^{20^\circ}_{4}\right)$ for three samples. The molecular refraction of limonene at 20° may, therefore, be calculated.

The value of the rotation given corresponds very closely to that noted by Kremers. The latter states that the rotatory power of limonene changes considerably on standing, giving, as an instance, a sample whose rotation had changed from $+121^\circ.3$ to $+103^\circ.23$. He also notes a corresponding increase in the specific gravity. I have found that a sample of pure limonene, sealed up in a flask which was nearly full, suffered no noticeable change after standing four months, but several samples of pure limonene which were kept in glass-stoppered bottles were found to decrease gradually in rotatory power; the same is true of phellandrene. The change is undoubtedly caused by oxidation of the terpene. One sample of limonene which originally had a rotation of +100°.6 stood for about a year in a partly filled, glass-stoppered bottle. It was then redistilled with steam. A considerable amount of nonvolatile matter remained behind and the distillate had taken on an odor resembling that of menthol. The oil was redistilled *in vacuo* and then showed a rotation of +100°.2. It distilled completely from 176°.5 to 177°.5.

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[1] The high number probably has its cause in the age of the resin; the product was notably more difficult to purify than any of the others. Unfortunately, several of the samples of pure limonene were used up before their physical constants had been accurately determined.

In this connection the behavior of limonene at elevated temperatures was also studied. Wallach[1] states that hesperidene (dextrolimonene obtained from oil of orange) is changed into dipentene by "*mehrstündiges*" heating at 250° to 270°, and a similar statement, probably derived from this source, appears in many of the books dealing with this subject.

(1) Twenty-five grams of pure limonene ($\alpha_D = 100°.7$) were heated in a sealed tube at 275° to 290° for five hours. The product was then distilled with steam. A small amount of nonvolatile matter, about 5 per cent of the original, remained behind. The polymerized product is only slightly soluble in alcohol. The distillate, after having been dried over solid potassium hydroxide, showed exactly the same boiling point as the original. Its rotation was +99°.8 and its refractive index was practically unchanged. A tetrabromide, prepared in acetic acid, after being recrystallized once from acetic ester, melted at 104°–105°, this being the melting point of pure limonene tetrabromide.

(2) The limonene obtained from the last experiment was heated, together with 2 or 3 drops of water, in a sealed tube at 290° for ten hours, the temperature rising to 360° for a short time. On examining the contents of the tube the water still appeared and the product was colorless. After distilling with steam, about 10 per cent was found to have been polymerized. The distillate, when dried, showed the same boiling point as before. The rotation had decreased a little: $\alpha_D^{30} = +97°$.

(3) Twenty grams of pure limonene, together with 2 drops

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[1] Ann. Chem. (Liebig), **227**, 289 (1885).

of water, were heated in a sealed tube at 200° for ten hours. The amount of polymerization was small. The boiling point was unchanged, as well as the refractive index, although the rotation had decreased 0°.5.

(4) Twenty grams of pure limonene, together wth 1 gram of benzoic acid, were heated in a sealed tube at 250° for seven hours. The product was extracted with a small amount of potassium hydroxide solution and all of the benzoic acid was recovered. It was then distilled with steam, only a small amount of residue remaining. After drying, the oil was redistilled and the boiling point found to be practically unaltered, although the rotation had decreased from +100°.1 to +98°.

(5) Twenty grams of practically pure limonene, together with 1 gram of acetone, were heated at 300° for six hours. The product was colorless. There was considerable polymerization. The boiling point of the oil was unchanged but the rotation had decreased from +98° to +96°.5.

(6) About 20 grams of pure limonene, with 2 grams aniline, were heated at 280° for seven hours. The product was extracted with very cold, dilute hydrochloric acid and distilled with steam. It then distilled completely from 176° to 177°. The rotation had decreased from +100°.2 to 99°.4.

(7) A few grams more of the pure substance were added to the limonene obtained from the last experiment and it was heated at 380° for six hours. The product was colorless. Approximately 15 per cent of the total had been polymerized. The boiling point of the distillate was unchanged, although the rotation had decreased to +93°.

It will be seen from the above experiments that if dipentene is formed from dextrolimonene at elevated temperatures the change is an extremely slow one. Even at 380° it would take many hours for its formation in sufficient amount to be detected. Moreover, it does not follow that a decrease in the rotation implies the formation of dipentene, although, from the unchanged boiling point, this seems probable. It will also be noted that the degree of polymerization is more than double that of inversion. From these experiments limonene is seen to be a very stable substance and almost indifferent to the influence of foreign reagents, even with respect to its optical activity. It may be distilled repeatedly at ordinary pressure without suffering alteration. It was found that after heating for eight hours in a tightly-stoppered distilling bulb in an oil bath at a temperature of 180° to 220° the distillate was identical in all respects with the original, except that its rotation had decreased by about 0°.2.

α-Phellandrene.

Reliable data concerning the terpene itself are wholly lacking. The physical properties recorded vary somewhat, but, with the exception of the rotation, do not differ greatly from those which I have found for pure phellandrene. Although phellandrene may be the predominant terpene in many of the fractioned products described in the literature, it must be remembered that the values of the physical constants of most of the terpenes of this series are very nearly equal to each other and as it appears often to be true that only terpenes of a certain class are to be found in the oil obtained from any one species, an admixture of a considerable percentage of one would have only a slight effect on the values of another. The optical rotation (α_D) of well-fractioned phellandrene products is seldom given as being higher than ±60°. Although phellandrene appears to be converted completely into the nitrite, it was found almost impossible to dry the filtered and well washed product so as to weigh it accurately. This difficulty is caused by the tendency of the crude substance to become slightly resinous. In solvents it undergoes rapid decomposition.

In nearly all of the terpene oils obtained in this work which were found to contain phellandrene, the latter was examined and found to be α-phellandrene, determined by isolating the α-nitrite described by both Schreiner[1] and Wallach.[2] The method usually employed was to dissolve the crude product, dried as well as possible by pressure between filter paper, in a very small amount of chloroform, then to filter to remove the

[1] Centrabl., **1901**, II., 544.

[2] Ann. Chem. (Liebig), **324**, 269 (1902); **336**, 9 (1904); **340**, 1 (1905).

water, and finally to precipitate the nitrite with ether; it was afterwards recrystallized once or twice from acetic ester. Wallach gives 112° to 113° as the melting point of the substance while Schreiner found 120° to 121°. During the first work which I did with this substance it was recrystallized from hot solvents and the melting point seemed to depend somewhat upon the solvents used. When acetic ester was employed the final melting point was always 113° to 115°. It was finally found that by dissolving the nitrite in acetic ester at 30° and then crystallizing in a freezing mixture, the melting point given by Schreiner was obtained. When the pure α-nitrite was again recrystallized from hot acetic ester, its melting point was lowered to about that found by Wallach. The latter used hot acetone in purifying his product, and the low melting point does not indicate that the substance with which he worked was impure. The conclusions drawn by Wallach from his work with this substance are based upon the assumption that it was free from chemical or physical isomers.

Rotation of the Nitrite.—The optical rotation found by Wallach for the α-nitrite obtained from two different sources was considerably higher than that found by Schreiner. In fact, the numbers given by Wallach for the same product show a considerable variation. Both workers used chloroform as a solvent. By the use of the same solvent I obtained a value agreeing very closely with that of Schreiner, the solution having stood for about ten minutes before the reading was made. It was found later that the reading diminished quite rapidly on standing.

(1) A solution of 0.35 gram of pure α-phellandrene α-nitrite, dissolved in 5 cc. of pure chloroform (Kahlbaum, best quality, shaken out repeatedly with water, dried over calcium chloride and then distilled), lost its optical activity entirely after standing for about four hours. The solvent was evaporated *in vacuo*. The residue did not crystallize until a small amount of ether was added, which evidently dissolved out some amorphous decomposition products. The recovered product, which was fully three-fourths of the amount used originally, was again dissolved in 5 cc. of fresh chloroform and

the solution was now found to be slightly levorotatory, the value being about one-tenth that of the original.

(2) A solution of 0.3 gram pure α-nitrite in 10 cc. of chloroform, after standing for eighteen hours, showed a positive rotation equal to about one-half that of the original negative value.

(3) A solution of 0.5 gram of pure α-nitrite in 3 or 4 cc. of chloroform was allowed to stand overnight. The chloroform was then removed, for the greater part, *in vacuo* and the residue treated with a small amount of ether. The solid residue was pressed out on a porous plate and again washed with ether. It consisted of a little more than 0.3 gram. When recrystallized from acetic ester it melted at 120° to 121° and the rotation of the recrystallized substance, roughly determined in dilute chloroform solution, was found to be about the same as that of the original pure α-nitrite.

(4) A saturated solution of the pure nitrite in acetic ester showed $\alpha_D = -6°.2$. A reading made some time later demonstrated that the rotation of the solution was decreasing. After standing overnight it had changed to $+1°.8$. The solvent was then removed *in vacuo* and the residue washed well with ether, only about one-fourth of the weight of original nitrite remaining. When this was recrystallized from acetic ester it melted at 119°.5 to 120°.5 and showed a rotation approximately the same as the original.

From the above experiments it seems certain that the change in rotation is not caused by a change of the dextro- into levo-α-nitrite, although, otherwise, the results obtained do not appear at all clear.

Wallach has shown that there is no change in melting point when the dextro- and levo-α-nitrite are mixed; hence the racemic mixture appears to be very similar to the active forms. It was desired to determine whether the varying rotation found for different samples of phellandrene could be explained by the presence of the racemic modification and it was thought that this could be determined from the rotation of the purified nitrite. In the case of the nitrite from oil XVII,A, purified, the value $[\alpha]_D^{30} = -126°.8$ at a concentration of 12.3 was found. The nitrite obtained from XIV,A, purified, gave $[\alpha]_D^{30} = -124°.5$ at a concentration of 8.84 Both readings were taken about ten minutes after the solutions were made, and from the rate at which the rotation was found to decrease, the immediate values would be about those found by Wallach. From this there appears to be no evidence that any racemic form of phellandrene is present in either of the two oils, the first of which had a value $\alpha_D^{30} = +73°.5$, and the second, $\alpha_D^{30} = +105°$. Later, another cause was discovered for this varying rotation of the phellandrene oils.

Stability of Phellandrene.—Wallach[1] recognized the fact that phellandrene is not a stable substance and recommended that it be fractioned *in vacuo*. Nothing further on the subject is to be found in the literature. It was ascertained that by distilling a sample of phellandrene at ordinary pressure, the rotation was lowered about 2°.

(1) The distilled product just mentioned was heated in a tightly stoppered distilling flask in an oil bath at 190° for eight hours, then distilled from the flask; about one-fifth of the total remained as a viscous residue almost insoluble in alcohol. The oil redistilled from 172° to 174°, which is a little higher than the boiling point of the original. Its rotation had decreased from +105° to +70°.

(2) The last distillate obtained was then sealed in a hard-glass tube and heated in an oven for twenty-four hours at 250°. The product was colored a slight yellow. It was distilled with steam, about 15 per cent of nonvolatile matter remaining behind. The distillate showed $\alpha_D^{30} = -25°.5$. It distilled completely from 171° to 176°.5. Phellandrene was no longer present and after careful trials no other terpenes could be identified. The oil had a very peculiar, benzenelike odor, which was quite different from that of any other terpene.

(3) The experiment was repeated with a fresh amount of the original sample of phellandrene. This time the heating was carried on at 225° for twenty-four hours. The product was colored slightly yellow. It was distilled with steam, a residue of nearly 25 per cent remaining behind. The distil-

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[1] Ann. Chem. (Liebig), **287**, 372 (1895).

late had the same peculiar, benzenelike odor and gave a very slight test for phellandrene. $\alpha_D^{30°} = -23.8$. It distilled completely from 171°.5 to 176°.5 and appeared to be identical with the product obtained in the last experiment.

(4) The combined residues obtained in this and the preceding experiments were distilled at 10 or 15 mm. A suitable thermometer was not used, so that the result of the distillation could be only roughly judged. A small amount of terpene oil passed over first, then a quantity of higher-boiling, somewhat viscous oil distilled before the temperature had risen much beyond 200°. Later, decomposition set in, the temperature went much higher, and the distillate was very viscous. It appears certain, however, that one of the polymeric products of phellandrene, probably a diterpene, may be distilled without decomposition.

In order to obtain evidence as to whether or not phellandrene is converted into the racemic form by heating, a quantity of very pure phellandrene (XVI,A, purified) was heated in a sealed tube at 200° for ten hours.

The product was distilled with steam and the distilled oil showed $\alpha_D^{30°} = +38°$. Phellandrene nitrite prepared from this in the usual manner melted at 119° to 120°.5 after the first recrystallization from acetic ester. In chloroform solution, at a concentration of 3, the specific rotatory power was found to be about the same as that produced in previous cases by the α-nitrite, and therefore there was no evidence that any racemic phellandrene had been formed.

After what has been brought out concerning the rapid change in rotation which the nitrite undergoes in solution, it must be borne in mind that the values obtained for this property of the nitrite are only approximate, but when they are taken for different samples under the same conditions, they are abundantly adequate for purposes of comparison.

The phellandrene used in the heating experiments (1), (2) and (3) was taken from sample XIV,A, purified, which, as will be brought out later, contained a small amount of levolimonene. The process was therefore repeated with a quantity of XVI,A, purified, which, so far as it was possible to determine, was pure phellandrene. The substance was heated in a sealed tube for forty-eight hours at 210° to 215°. The product was colorless. The oil, after having been distilled with steam, still gave a slight test for phellandrene and showed $\alpha_D^{30} = -18°$. The levorotation of the product appears, therefore, to be due to a product of isomerization of phellandrene. This oil, when dissolved in cold carbon tetrachloride and treated with bromine, combined at once with less than 2 atoms of the latter and considerable hydrobromic acid was evolved. Further action was much slower. The same result was obtained in glacial acetic acid, although in this case the evolution of hydrobromic acid was not so apparent, as it was probably held in solution by the acetic acid.

A portion of the same sample of freshly purified phellandrene used in the last experiment was sealed in a flask which was nearly full and allowed to stand for three months. The original rotation was $\alpha_D^{30} = +129°.8$. On opening the flask it was found to be $\alpha_D^{27.5} = 127°.1$, hence a decrease of about 3°. Phellandrene, therefore, undergoes a slow alteration at ordinary temperatures, probably the same which takes place more rapidly at a higher temperature.

Action of Hydrochloric Acid.—About 30 grams of phellandrene, taken from the oil V,A, purified, were heated with metallic sodium for a few minutes, then distilled from the metal into a dry fractioning flask. $\alpha_D^{30} = +115°.5$. It was mixed with an equal volume of dry carbon disulphide and a slow stream of very dry hydrochloric acid was then passed into the liquid, the exit tube having been attached to a tube of calcium chloride. The acid was readily absorbed and the liquid appeared to become heated more quickly than when limonene had been employed under the same conditions. It was kept cool by immersing the flask in a dish of water. After four or five hours, the absorption appeared to be nearly complete, but the current of acid was continued for several hours longer. The contents of the flask were then distilled at reduced pressure. After the excess of acid and the carbon disulphide had been removed, the residue was distilled at as low a pressure as could be maintained, considering that hydrochloric acid appeared to be given off continually. The product distilled completely within a range of 15° or 20°; the distillate contained much terpene and possessed a very strong odor of hydrochloric acid. Phellandrene behaves quite differently from limonene, and the hydrochloride which appears to be formed at ordinary temperature is decomposed to a large extent by distillation at reduced pressure.

Action of Bromine.—Several investigators have studied the action of bromine upon oils containing phellandrene, and from their work it appears that the substance takes up at once only 2 atoms of bromine to form an oily dibromide. It was desired to ascertain whether this dibromide, when prepared from pure phellandrene, could be obtained in the crystalline form.

Three and one-tenth grams of phellandrene, taken from sample XVI,A, purified, were dissolved in 3 volumes of carbon tetrachloride and the solution cooled in a freezing mixture; 3.4 grams bromine (2 atoms), dissolved in 3 volumes of the same solvent and cooled, were then slowly added to the first solution, which was continuously shaken, while immersed in the freezing mixture. The color of the bromine disappeared immediately, until nearly all had been added; the last few drops produced a color which remained for over one minute and fumes of hydrobromic acid then appeared. The solution was then evaporated *in vacuo* for several hours in order to remove the solvent completely. The residue, a quite mobile oil, was allowed to remain in the ice chest for twenty-four hours, but did not crystallize.

Crystalline Auto-oxidation Product of Phellandrene.—It was frequently observed that samples of purified oils, on standing, deposited crystals upon the walls of the containing vessel. The same thing has been noted, in working with elemi oil, by Tschirch and Cremer and also by Wallach, who connected the crystals with the solid constituents of the resin. In most cases, even after long standing, the amount of crystalline substance was small in proportion to that of the oil, but in several instances about 0.2 gram was obtained from 50 to 75 grams of oil. One sample of purified, high-boiling oil, not over 25 grams in amount, deposited nearly 0.5 gram of this crystalline substance soon after distillation. It was later observed that in no case were crystals found in an oil derived from a sample of elemi known not to contain phellandrene. Although, at this time, some of the oils had been completely used up, it was observed that more or less of the crystalline substance could be found in both the terpene and the high-boiling oils on hand which were derived from samples containing phellandrene. It seems almost certain that the substance is derived from phellandrene. In all cases which were studied, the crystals from different oils were found to be identical. They are moderately soluble in alcohol and acetic ester, sparingly in ether and chloroform, and almost insoluble in petroleum ether. They are best purified by recrystallization from hot acetic ester, from which solvent they separate, on cooling, as fine needles, melting at 164°.5 to 165°.5. In most cases they were pure after the first crystallization. In the condition in which they are found in the oil, the crystals are colorless, hexagonal prisms, generally of good size; two of the largest weighed, when taken together, just 1 centigram.

I. 0.1667 gram substance gave 0.4322 gram CO_2 and 0.1607 gram H_2O.

II. 0.0713 gram substance gave 0.1853 gram CO_2 and 0.0708 gram H_2O.

	Required for $C_{10}H_{18}O_2$.	Found. (1).	Found. (2).
C	70.59	70.71	70.87
H	10.59	10.71	11.03

The substance is probably a dihydroxyphellandrene. That it is of the simple formula given, rather than a polymer, is indicated by the fact that it sublimes very readily when it is heated below its melting point.

As to the physical constants of phellandrene, the values obtained from XVI,A, purified, should be given preference. Those of several of the other samples, most of which, it will be seen later, contain small amounts of levolimonene, are also given in the following table, there being, of course, very little difference except in the degree of rotation.

Purified product.	Boiling point, complete.	α_D^{30} +	n_D^{30}.	Sp. gr. $\frac{30}{4}$.	Boiling point at reduced pressure.	mm.
XVI,A	172–173.5	129.8	1.4695	0.8324	89.3–90.8	56.5
V,A	172–174	122.6	1.4698	....	82.7–84	43.5
XIV,A	....	105.1	1.4694	0.8322		
XVIII,A	172–173.5	113.5	1.4696	0.8330		

Each of two determinations gave the specific gravity at $(\frac{30°}{4})$ as being 0.0075 less than that at $(\frac{20°}{4})$.

The boiling point of phellandrene is seen to be about 4° lower than that of limonene; the specific gravity is a little less, while the index of refraction is somewhat higher.

In determining the constitution of phellandrene, Wallach[1] has recently deduced the molecular refraction of the substance, deriving his value from the phellandrene obtained from elemi oil by fractionation. From the present work it can be seen that this "phellandrene" was partly limonene, although it can also be seen that the limonene would have little influence upon the value obtained.

Classification of the Terpene Oils.

(1) Of the 21 samples of resin examined, 10 gave pure dextrolimonene.

(2) Nine of the remaining oils, including all but the two optically inactive ones, contained more or less phellandrene. These nine oils fall into two classes.

(*a*) Those showing an initial boiling point decidedly lower than that of phellandrene and possessing a peculiar, indefinable odor. These are the oils from *Samples VII.*, *X.* and *XV.*, and all are dextrorotatory. The oil from *Sample X.* has the lowest initial boiling point and its rotation is decidedly the smallest. The data obtained for the physical constants of these oils do not lead to any decided conclusion, but it appears extremely improbable that any body like pinene is present in them. From the marked regularities which are found to exist in the different samples, it seems very probable that we have present in these three cases one of the unidentified terpenes of the limonene series.

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[1] *Loc. cit.*

(*b*) Of the remaining six oils containing phellandrene, obtained from *Samples V., XI., XIV., XVI., XVII.* and *XVIII.*, one was levorotatory, and the others, although they were all highly dextrorotatory, showed considerable variation in rotation. The two giving the greatest variation also had a slightly higher boiling point, while the others, to judge from their boiling point, appeared to be pure phellandrene. As has already been brought out in the discussion of *Sample XI.*, the terpene oil derived from it consisted largely of levolimonene.

In summing up this work it was suspected that the variation in the rotation of the other phellandrene oils was due to the presence in them of small amounts of levolimonene which could not be detected. As shown in the experimental work which is detailed just below, the presence of levolimonene could readily be proved by the addition of a small portion of dextrolimonene to the oil and the subsequent isolation of dipentene tetrabromide. The presence of levolimonene was proved in oils XVII,A, purified, and XVIII,A, purified. XIV,A, purified, had been used up in previous work. In V,A, purified ($\alpha_D = +122^\circ.6$) and XVI,A, purified ($\alpha_D = 129^\circ.8$), it cannot be definitely concluded whether or not levolimonene was present, and it can be readily seen that if present at all it was in very small amounts.

Detection of Levolimonene.—A portion of XVII,A, purified, was added to one-tenth its weight of dextrolimonene and 0.45 gram of the mixture was treated in a freezing mixture with bromine in amyl alcohol and ether. Crystals soon began to separate, and after 3 hours they were filtered and washed with a small amount of alcohol. The yield was 0.65 gram. After one recrystallization from a mixture of alcohol and acetic ester, the product melted at 124° to 125° and was, therefore, dipentene tetrabromide.

Four grams of XVIII,A, purified, were mixed with 0.4 gram of dextrolimonene and treated with bromine as before. After the product had stood overnight, 0.2 gram of crystalline bromide was obtained, this being only about one-third of the amount isolated in the previous case. After recrystallization from a mixture of alcohol and acetic ester the body melted at 124° to 125° and was accordingly pure dipentene tetrabromide.

Both V,A, purified, and XVI,A, purified, the former, at least, presumably containing a very small proportion of levolimonene, were treated with 15 per cent of their weight of dextrolimonene and brominated in the usual manner. In neither case had a trace of the crystalline product separated after twenty-four hours, but in each instance, after two or three days, a small quantity of crystals appeared which, after recrystallization, melted at about 124°. No great significance is attached to this for it was found that XVII,A, purified, when it was brominated without the addition of limonene, after standing for several days, yielded a very small amount of crystals which had about the same melting point; the appearance of dipentene tetrabromide in these cases is possibly due to the continued action of hydrobromic acid upon limonene tetrabromide.

(3) The two remaining samples of resin gave almost optically inactive oils, which were found to be terpinene and terpinolene.

High-boiling Oils.

The high-boiling oil contained in distillates B and C of the resin was found in most cases to consist chiefly of a constant-boiling product. By distilling twice *in vacuo*, a number of such products were obtained and it was found that the boiling point was almost the same in all cases, 167° to 170° at 35 mm. In some cases it was 1° or 2° higher or lower. In all of their other properties, however, these oils showed marked differences. The data derived from them are placed in the table below in order to make plain the relation existing between them.

In this table every measurement which has been made is recorded. In a few cases, especially with the older samples of resin, it was found impossible to obtain a constant-boiling product from the crude distillate, and in other instances no high-boiling distillate was taken.

Designation of oil.	Sp. gr. $\binom{30}{4}$	α_D^{30}	n_D^{30}	Appoximate solubility in 100 parts 55 per cent alcohol (by volume).
IV,C, purified	1.0315	—1°.2	1.5159	16
I,C, purified	1.0247	±0°.0	1.5143	....
XIII,B, purified	0.9969	—0°.5	1.5068	....
III,B, purified	0.9887	—2°.5	1.5055	7.5
VII,C, purified	0.9689	—2°.5	1.5005	....
VI,B, purified	0.9621	....[1]	1.4995	....
VIII,B, purified	0.9559	—2°.4	1.4985	4
XVIII,B, purified	0.9559	+2°.0	1.4950	....
II,C, purified	0.9522	—2°.7	1.4973	....
XIV, B, purified	0.9482	—2°.0	1.4957	....
XVI,B, purified	0.9461	—0°.8	1.4944	3
XII,B, purified	0.8677	+71°.6	1.4757	3

The oils are arranged in the order of their specific gravities and it will be seen at once that the indices of refraction arrange themselves in precisely the same way, with the exception of XVIII,B, purified, which has an index about 0.0035 lower than it should have. This same oil is also exceptional in that it is slightly dextrorotatory, while all the others are slightly levorotatory. All the oils are practically optically inactive excepting XII,B, purified, which stands apart in all respects from the others.

Analyses of XII,B, purified, gave the following results:

I. 0.1455 gram substance gave 0.4309 gram CO_2 and 0.1503 gram H_2O.

II. 0.1490 gram substance gave 0.4405 gram CO_2 and 0.1534 gram H_2O.

		Found.	
	Required for $C_{15}H_{26}O$.	(1).	(2).
C	81.08	80.77	80.63
H	11.71	11.48	11.44

The analyses are in tolerably good agreement with the formula assigned. The substance, which had remained as an oil for three months after purification, became solid when the inside of the bottle was scratched with a glass pipette. It dissolved in all the organic solvents in any proportion and when an attempt was made to recrystallize it from dilute alcohol in the cold, it separated as an oil. The body is almost colorless and possesses a mild, pleasant odor. It is moderately viscous. At ordinary pressure it distils at 270° to 280° with the formation of water.

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[1] Not determined.

A half-dozen or more substances containing oxygen, mostly crystalline, have been isolated from the high-boiling portions of different essential oils. They have, in general, the same properties as this body, and to most of them the same chemical formula has been assigned. They are sometimes known as sesquiterpene alcohols. To judge from the data given in the above table, the body is radically different from any of the other constant-boiling products isolated from different samples, and, as will be seen later, it is not a constituent of any of these oils. It is evidently practically a pure substance and its occurrence in this single sample is most remarkable.

All of the other oils given in the table are closely related and are grouped together. In addition to the regular variations already noted, there is a constant increase in viscosity from the first oil to the last. The first, IV,C, purified, is very mobile, while the last, XVI,B, purified, is very viscous. All of these regularities at once suggest that we have in these different products a mixture of two substances in varying proportions and this is undoubtedly the case. The following analyses tend to confirm this view. The values obtained for XVI,B, purified, are as follows:

I. 0.1911 gram substance gave 0.5533 gram CO_2 and 0.1934 gram H_2O.

II. 0.1630 gram substance gave 0.4721 gram CO_2 and 0.1637 gram H_2O.

	Found.	
	(1).	(2).
C	78.96	79.00
H	11.24	11.16

The analysis of XIV,B, purified, gave the following results:

I. 0.1482 gram substance gave 0.4286 gram CO_2 and 0.1460 gram H_2O.

II. 0.1580 gram substance gave 0.4547 gram CO_2 and 0.1589 gram H_2O.

III. 0.2116 gram substance gave 0.6132 gram CO_2 and 0.2137 gram H_2O.

	Found.		
	(1).	(2).	(3).
C	78.87	78.49	79.03
H	10.95	11.17	11.22

The values obtained for III,B, purified, are as follows:

I. 0.1683 gram substance gave 0.4629 gram CO_2 and 0.1533 gram H_2O.

II. 0.1714 gram substance gave 0.4709 gram CO_2 and 0.1500 gram H_2O.

	Found.	
	(1).	(2).
C	75.01	74.93
H	10.12	9.72

IV,C, purified, gave the following values:

I. 0.1504 gram substance gave 0.3917 gram CO_2 and 0.1163 gram H_2O.

II. 0.1887 gram substance gave 0.4917 gram CO_2 and 0.1420 gram H_2O.

III. 0.2388 gram substance gave 0.6245 gram CO_2 and 0.1850 gram H_2O.

	Found.		
	(1).	(2).	(3).
C	71.03	71.07	71.32
H	8.59	8.36	8.79

Analysis III. was made on a middle fraction of the substance, redistilled in a vacuum.

If we consider that these oils belong either to the terpene or sesquiterpene class, and are composed of substances having the formula $C_{10}H_{16}$ or $C_{15}H_{24}$, or of their oxygen derivatives, and consider also their boiling points, we have, in general, three possibilities: (1) a sesquiterpene, or (2) a dioxygen derivative of a terpene, or (3) a monoxygen derivative of a sesquiterpene may be present. The sesquiterpenes are almost insoluble in dilute alcohol; the solubilities in 55 per cent alcohol (by volume), respectively, of pure cadinene prepared from the hydrochloride and pure cedrene distilled from oil of cedar were determined and found to be practically *nil*. The different high-boiling oils from elemi were then tested with the result that they showed a considerable solubility in 55 per cent alcohol; this solubility, which, in several instances, is given in the table, varied just as do their other properties. In a few instances there was evidence of a trace of sesquiterpene, but the amount was inconsiderable. That the soluble constituents of the oil would have no great effect upon the solubility of a sesquiterpene, if such a substance were present, was shown by adding a small amount of the latter to several of the clear solutions.

The solubility of oil XVI,B, purified, the last one of the series, is very close to that of the pure sesquiterpene alcohol XII,B, purified (see p. 645), so that the assumption that we have here a substance similar to the latter seems to be verified. Moreover, the analysis of XVI,B, purified, shows that its composition is close to that of a sesquiterpene alcohol. On the other hand, the member at the other extreme of the series IV,C,purified, has a much greater solubility in 55 per cent alcohol, this property being remarkable. Considering the analysis and the boiling point, the latter substance appears to be a dioxygen derivative of a terpene and is nearly pure; all of its properties are in accord with this assumption. The values obtained on analysis show so great a difference from any formula which can be calculated for the oil that it cannot be considered pure. The formula $C_{10}H_{14}O_2$ requires 72.28 per cent for carbon and 8.44 per cent for hydrogen. This oil is slightly yellow in color, of a very mild, pleasant odor, and is perfectly miscible with all the solvents. It redistilled from 275° to 279° at ordinary pressure, with the formation of water.

The other oils are all more or less yellow in color. Because of the great viscosity of the oils in the lower part of the series and also because of their lack of optical activity, it seems certain that the sesquiterpene derivative contained in them is quite different from the optically active substance XII,B, purified.

Amyrin.

The crystalline residue obtained from elemi by treating it with alcohol has been worked with by many chemists and has long been known as amyrin. Baup,[1] who appears to have employed Manila elemi in his work, gives 174° as the melting point of the substance. Vesterberg,[2] who also used Manila elemi, was unable to obtain a constant melting point and showed that the substance is a mixture of two very similar bodies, which were separated by means of their acetyl derivatives; these bodies are α-amyrin, melting point, 180° to 181°, and β-amyrin, melting point, 193° to 194°. Tschirch and Cremer give 170° to 171° as the melting point of amyrin from Manila elemi after repeated crystallization.

I wished to note if there was any variation in the amyrin obtained from individual samples of elemi; it was thought that possibly α-amyrin or β-amyrin might be found in pure condition, when derived from the resin of a single tree.

Two samples, VIII., from which had been isolated pure limonene, and XVIII., which had yielded almost pure phellandrene, were examined. In neither case could a body of constant and sharp melting point be obtained; the products resulting from several recrystallizations behaved as mixtures, although, comparatively, they melted at about the same temperature.

This work was carried on in Manila in the chemical laboratory of the Bureau of Science of the Philippine Government.

ON THE THEORIES OF INDICATORS.

By S. F. Acree.

In a conference, Professor Stieglitz has convinced me that his attitude towards the chromophoric theory of indicators, as expressed in his article of 1903, has remained the same as that which he postulated in our interview in September, *viz.*, that the idea of simple quinoid chromophores requires amplification on the basis of intermolecular quinhydrone formations for phenolphthalein, rosaniline and similar dyestuffs. He has shown me now that his refutation, in his March article,[1] of my charge of "wrong ideas" was limited to the alleged "wrong idea" of overlooking the ionization of the phenol groups in phenolphthalein. It is clear now, from a statement of his experimental work, not yet published, that he includes the phenol salts of these indicators in his quinhydrone hypothesis. I was not aware of that fact when I wrote the April article.[2] Professor Stieglitz therefore developed the idea of quinhydrone formation in such types as rosolic acid, alizarin, eosin, phenolphthalein, etc., as I pointed out in April,[3] and from this developed the idea of the quinhydrone salts. Professor Stieglitz credits me for the idea of tautomeric mono- and dibasic salts of phenolphthalein, etc., and for the development of the idea of quinhydrone salts, suggested by Baeyer[4] and Hantzsch,[5] from our idea of tautomeric salts and the work of Baeyer,[4] Hantzsch,[5] Baly,[6] and Jackson and Oenslager[7] and Jackson and Clarke.[8] It is evident, therefore, that we reached similar conclusions from these two different starting points.

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[1] Jahres. d. Chem., **1851**, 528.

[2] Ber. d. chem. Ges., **20**, 1243 (1887); **23**, 3187 (1890).

The similarity of our views concerning the constitution of these colored salts, as well as the points of difference, make it seem best that my April article be considered a joint article by J. Stieglitz and S. F. Acree, expressing the independent views and conclusions of each of us, and I request that it be reviewed and indexed as such. Mr. Stieglitz has agreed to this arrangement, proposed by me as soon as my attention was called to the true circumstances. By agreement I shall investigate the problem chiefly from the standpoint of the alkylation reactions and Professor Stieglitz is investigating the color phenomena as affected by the equilibrium conditions, the need for which was brought out by me in April.

JOHNS HOPKINS UNIVERSITY,
April 25, 1908.

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[1] THIS JOURNAL, **39**, 429.

[2] *Ibid.*, **39**, 528.

[3] *Ibid.*, **39**, p. 529, footnote.

[4] Ann. Chem. (Liebig), **354**, 162 (1907).

[5] Ber. d. chem. Ges., **39**, 1089, 1095, 3076, 3080 (1906); *Ibid.*, **40**, 333, 1527 (1907).

[6] J. Chem. Soc., **85**, 1029; **89**, 502, 514; **91**, 426, 1572.

[7] THIS JOURNAL, **18**, 1.

[8] *Ibid.*, **34**, 441.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

THE THEORY OF INDICATORS.

By Julius Stieglitz.[1]

Professor Acree, in his article on the Theory of Indicators,[2] has brought out quite thoroughly and sufficiently the reasons which lead me also to the conclusion that the chromophoric theory of indicators (the "simple quinoid theory," as it may be termed for convenience), as given in my article in the *Journal of the American Chemical Society* in 1903,[3] required amplification, and that it required amplification on the basis of the idea of intramolecular quinhydrone combinations for phenolphthalein, rosanilines and similar indicators and dyestuffs.[4]

By some misunderstanding—our discussion of the subject was comparatively brief—Dr. Acree did not know that I included in the quinhydrone hypothesis the effect of alkalies as intensifying the color of phenol indicators (rosolic acid, etc.), as they do that of quinhydrones. This fact being one of daily experience with me—I had been working for two years with alizarin, alizarinsulphonate and rosolic acid—was not emphasized by me, but taken for granted. It was really one of the main reasons for my not being satisfied with the old "simple quinoid hypothesis;" the latter did not include any rational explanation of the intense change of tint of this class of indicators when alkali is added. In alizarins, rosolic acid, etc., we have a quinoid group *ab initio* and yet the color is enormously intensified by the addition of alkali. This effect was formerly considered to be due simply to "auxochromic" influence of the phenol groups and their salts, according to the current ideas, without any attempt to develop an explanation of such well-known "auxochromic" results. The quinhydrone hypothesis seemed to me the most rational explanation of this change of color because I was familiar with Jackson's important observation[1] that the alkali salts of quinhydrones (phenoquinones) are even more intensely colored (blue) than are the corresponding quinhydrones themselves; this observation had been impressed on me so much the more since in his first paper Jackson refers to my work[2] on a related compound, dichlorquinonedimalonic ester, a body which in 1891 I had found to change from a pale-yellow tint to permanganate purple when treated with alkali, and to a deep blue when treated with ammonia. It was the combination of these results of Jackson's with the well-known characteristic behavior of rosolic acid and also with the behavior of the phenol and carboxylic esters of phenolphthalein and its derivatives that ultimately led me to the conviction that intramolecular quinhydrone formation is really the cause of the intense coloration of our phenol derivatives when used as indicators with alkalies. Another possibly important factor has been brought out recently by Torrey's[3] and Hantzsch's[4] investigations on the colored phenol silver salts. Green's[5] discovery of last September that the carboxyl ester of phenolphthalein is orange and that alkalies convert it into a violet salt confirmed me, it may be said, in my conclusion that I was on the right track:

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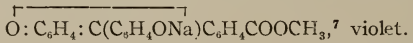
[1] See the preceding article in this number of This Journal.

[2] *Ibid.*, **39**, 528 (1908).

[3] **25**, 1119.

[4] This Journal, **39**, 431, footnote. *Ibid.*, **39**, 529, footnote 2, first two lines.

$$O:O_6H_4:C(C_6H_4OH)C_6H_4COOCH_3,^{6} \text{ orange};$$



$$O:C_6H_4:C(C_6H_4ONa)C_6H_4COOCH_3,^{7} \text{ violet}.$$

I will not take space here to dilate on my views concerning the quinhydrone hypothesis, but will reserve this to a more fitting occasion; I agree in the main points with the development of the equations by Professor Acree.[8] I will say, however, that an adequate theory must account for the greater intensity of color of quinhydrones *versus* simple quinones;

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[1] THIS JOURNAL, **17**, 588; **18**, 1, etc.

[2] *Ibid.*, **13**, 38 (1891).

[3] Torrey and Hunter: Ber. d. chem. Ges., **40**, 4332 (1907).

[4] Hantzsch and Scholtze: *Ibid.*, **40**, 4875 (1907).

[5] Green and King: *Ibid.*, **40**, 3724 (1907).

[6] This is probably an intramolecular quinhydrone in equilibrium with the body of the structure given, as is probably the case for rosolic acid.

[7] This probably has a modified structure, involving the formation of a *second quinoid complex* of the phenolate group.

[8] *Loc. cit.*

it must account for the still greater intensity of color of the metal salts of the quinhydrones, and also for the significant fact recorded by Jackson that aliphatic alcohols form *colorless* addition products with quinones; in that last fact lies, I believe, the key to the correct solution of the whole problem, the necessary second (and third) phenol groups giving us the nuclei for the formation of new (quinoid) chromophores. Only extensive qualitative and particularly quantitative work on the questions of equilibrium and stability involved can give the necessary experimental basis for a final solution, as has also now been brought out by Acree. It was the wish to bring such experimental material which has delayed the publication of my views—a result now accomplished by the joint paper with Professor Acree.

REPORTS.

IONIUM, THE PARENT OF RADIUM.

A Review of Recent Investigation.

It has always been felt necessary to suppose that the continual breaking down of radium into radium emanation and α-particles is compensated, in the natural ore, by a continual regeneration; in fact that the supply is kept up by the breaking down, also continuous and spontaneous, of another substance by which radium is produced. The existence of radium at the present day presupposes a parent, as the perturbations of Saturn predicted the undiscovered Uranus and Neptune.

It is true that the rate of decay of radium is so slow, compared to the duration of laboratory experiments, as to be almost negligible, yet in proportion to the hundreds of thousands, or millions, of years by which geologists measure the age of deposits, it is so rapid that no original supply of radium, even in veins of pleistocene age and all but the most recent of the 'recent' formation, could have survived to the present time. If we take the highest estimate for the decay period, *i. e.*, that about 3000 years is required for any quantity of radium to be reduced to one-half, it is easily seen that as the decay follows an exponential law, in $x \times 3000$ years the amount will be reduced to $\frac{1}{2^x}$. Putting, for example, $x = 22$ we see that in 66000 years a mass of ore which was originally pure radium would be reduced to a content of about one part in four millions, or a quarter of a gram per ton, which is about that of the richest pitchblende as it now exists, while in another 60,000 years this minute amount would be again reduced a million times. It is plain then that radium itself must be a link in a chain of radioactive disintegration, such as has been fully investigated in the case of the more quickly decaying radium emanation and its products, radium A, B, C, D, E and F. As in that case, so here, each member of the series accumulates by the breaking down of its predecessor until its own rate of decay exactly counterbalances its formation, after which the amount present remains in a constant proportion to the amount of its parent. The proportion of substances in this state of *radioactive equilibrium* must obviously be the inverse of that of their rates of decomposition (or directly equal to that of their decay periods) and the time taken to reach a state of practical equilibrium may be put at about ten times (since $\frac{1}{2^{10}}$ is slightly less than 0.1 per cent) the decay period of the substance formed.

With the help of this theorem we can readily determine the amount of radium in any substance by measuring the activity of the emanation which exists in it in radioactive equilibrium, provided that the substance has not been subjected to chemical treatment for a previous period of about forty days (the decay period of the emanation being 4 days). Analyzing in this way twenty-two specimens of uranium ores containing from 0.3 to 75 per cent of uranium, Boltwood found a strikingly constant proportion between the amounts of uranium and radium present.[1] His conclusion confirmed a previous suggestion by Rutherford and Soddy[2] that radium was formed by the decomposition of uranium. The constant proportion, itself a necessary consequence of the law of radioactive equilibrium, could be satisfactorily accounted for in no other way.

Since every gram of radium is accompanied by nearly three million grams of uranium, it follows that the latter decays so slowly, taking over a thousand million years to fall to half its value, that we may regard its amount as approximately constant throughout geological time. So delicate however, is the electroscopic method of testing for radium that as little as 10^{-12} gram can be detected with reasonable certainty, an amount which should be generated by a kilogram of uranium, when in radioactive equilibrium, in about a quarter of an hour. This was tested by Soddy, Whetham and Boltwood, using different methods to purify their uranium, with varying results. One fact was, however, made plain by all three, that the rate of growth was certainly far below, and probably less than a thousandth part of the value just calculated. The necessary conclusion is that uranium does not generate radium directly, but first produces an intermediate product with a fairly slow rate of decay. Not till this has accumulated for many years, perhaps centuries, will radioactive equilibrium be established and the rate of growth of radium reach the above value. The known transition product, uranium X, with its small decay period of 22 days, does not materially affect the question; for slow changes we may regard the decay of uranium X as if it were identical with the uranium whose history it so closely follows.

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[1] Phil. Mag. [6], 9, 599 (1905).

[2] *Ibid.* [6], 5, 590 (1903).

Researches actively carried on in several quarters for the last three years in the hope of finding this missing link have recently been crowned with success. Boltwood announced[1] in November, 1906, that he had isolated from a uranium mineral a small quantity of a substance, which he took to be actinium,[2] which more than doubled its radium content in six months. Starting with the precipitate carried down by a little thorium oxalate in a solution of 1 kg. of carnotite, a rate of growth of radium was observed equivalent to 1.6×10^{-8} gram per year. This would suffice to maintain equilibrium with the 7.6×10^{-6} gram radium which, by calculation, existed along with the 200 grams uranium in the ore, if the decay period of radium is 3100 years, which agrees closely with other determinations.[3] This would show that the immediate parent of radium was present in the precipitate. Rutherford[4] confirmed this observation but pointed out that the substance in question could not be actinium, owing to the insufficient activity of the latter on the hypothesis that all the radium in ores is derived from it. For the activity of any substance in radioactive equilibrium must bear a fixed proportion to that of any other substance in the series, and this proportion can be approximately calculated from the number of steps in the series of changes in which α-particles are given off. For the velocity of these particles, the chief cause of the ionization of the air observed by the electroscopic test, does not vary greatly, while the number lost from a molecule at each change in which they are expelled is constant (probably *one* each time). Now, as we have seen, in a state of equilibrium the same number of molecules of *each substance* is formed and destroyed per second, the greater or slower rate of decay of the several substances being exactly compensated by the smaller or larger proportion in which they are present. Thus, for example, the activity of radium and its products of decomposition, four of which give out α-particles, must together be about five times that of the same radium when freshly prepared, a proportion which agrees with experimental determinations. Now the activity of the actinium present in a uranium mineral is only a small fraction of that of the radium. Again the last known product of actinium degradation, Act. B, failed in Rutherford's hands to give more than a fifth, at most, of the calculated quantity of radium. In a later letter[1] Rutherford states that he has separated from his actinium by ammonium sulphide a fraction about 100 times as active as the original preparation, yet showing no appreciable growth of radium in 80 days. The radium parent, therefore, a substance chemically quite distinct from actinium, accompanies the latter in commercial specimens, and is more readily carried down by the sulphur precipitated from the thiosulphate in the (old?) ammonium sulphide. Radioactinium, the first product of the decay of actinium[2] and the probable cause of all its activity, is also relatively more concentrated in the precipitate, causing a rise of activity to twice its value in 20 days; but no corresponding change in the rate of growth of radium could be detected. Boltwood[3] accepts Rutherford's conclusion, confirming it by showing that 0.4 gram of a preparation of his new substance some weeks after separation, "sufficient to give a leak of 500 div. per min. in an α-ray electroscope, did not produce sufficient actinium emanation to permit its detection in another electroscope of greater sensitiveness." No rise in activity was observed corresponding to the formation of actinium X, nor could this be separated by ammonia; sulphur from a thiosulphate did not carry down any radioactinium from a preparation which was five months old. The rate of growth of radium was constant within the limits of experimental error for 500 days, from which we may conclude that the period of decay of the new substance is at least of the order of magnitude of radium

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[1] Nature, **75**, p. 54.

[2] Identical with Giesel's "Emanium." Debierne: Compt. rend., **139**, 538 (1904).

[3] Ramsay and Cameron (J. Chem. Soc., **91**, 1266 (1907)) alone find a decidedly lower value, about 200 years.

[4] Nature, **75**, 270.

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[1] Nature, **76**, 126. See also Phil. Mag., **14**, 733.

[2] See Hahn: Nature, **73**, 559 (1906).

[3] Nature, Sept. 26th, 1907. Also Am. J. Sci., **24**, 370.

D (12 years),[1] and its rate of growth from uranium (*i. e.*, from UrX) correspondingly slow.

Ionium, as Boltwood has named it, from the *ions* it produces, is chemically analogous to thorium and is precipitated along with it by oxalic acid, redissolving in ammonium oxalate, while actinium more nearly resembles lanthanum.[2] No method of separation from thorium has yet been given. It is characterized by α-rays of unusually short range, about 2.8 cm. in air;[3] its β-radiation is also more easily absorbed than that from uranium, the aluminium coefficient being 1.8. Agreeing with this, its activity is only about 0.7 to 0.8 of that of the equilibrium amount of radium. It gives no emanation.

A confirmation of all these properties is given in a note by Marckwald and Keetman.[4] Their method of extraction from pitchblende or autunite was to dissolve the ore in nitric acid, to convert into sulphates, filtering off those of lead, barium and radium, and to add hydrofluoric acid, which gave a very active precipitate, consisting chiefly of cerium, yttrium and thorium fluorides. These were dissolved by digesting with sulphuric acid and the thorium precipitated by oxalic acid. Ammonium carbonate, like the oxalate, redissolves ionium along with thorium, from which it follows that pitchblende residues must be relatively free from ionium, which is to be looked for in the uranium mother liquors.

Working from an entirely different standpoint, Hahn[5] has reached the same conclusion. In examining thorium preparations for the intermediate decomposition products, mesothorium[6] and radiothorium,[7] he found that commercial "pure" thorium salts contain considerable amounts of radium, though made from monazite which contains very little uranium. The amount of radium was greater the older the specimen, samples from 1 to 7 years old containing from 0.5 to 4×10^{-9} gram per 100 grams thorium. Direct experiment proved that the amount in a freshly prepared specimen of thorium nitrate was doubled in 2 months. When the thorium was precipitated as oxalate, the radium in the filtrate showed no increase in 4 months, in which time also 1 mg. of radiothorium, with an activity of about 100,000, prepared by precipitating barium sulphate in a solution of thorianite, showed no increase in its small radium content. The radium parent, which is quite distinct from and independent of thorium, is thus seen to be concentrated in the process of manufacture of thorium salts (a trade secret). Assuming that none is lost and that the sand contains 0.3 per cent uranium to 5 per cent ThO, Hahn calculates that the observed growth of radium would maintain in equilibrium the amount which should theoretically accompany the uranium of the ore, if the decay period is 2600 to 3200 years.

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[1] Meyer and Schweidler: Physik. Z., **8**, 457 (1907).

[2] Giesel: Ber. d. chem. Ges., **40**, 3012.

[3] Nature, Oct. 10th, 1907. Am. J. Sci., **25**, 289.

[4] Ber. d. chem. Ges., **41**, 49 (1908).

[5] *Ibid.*, **40**, 4415.

[6] *Ibid.*, **40**, 1462 and 3304.

[7] P. Roy. Soc., **76**, 115 (1905). Jahrbuch d. Radioact., **3**, 330.

The existence of ionium, the parent of radium, may therefore be considered as proved. A paper by Boltwood on his discovery is announced for the May number of the *American Journal of Science*.

B. B. Turner.

THE ATOMIC WEIGHT OF TELLURIUM.

In a recent number of the *Berichte*,[1] W. Marckwald points out that the question of the exact atomic weight of tellurium has been under constant discussion and investigation since the Mendeléeff-Meyer arrangement of the elements in the Periodic System was first suggested, for in the case of this element the position assigned to it from a study of its chemical properties is not in agreement with the rule that the elements are arranged in the order of increasing atomic weights, as tellurium, with a higher atomic weight than iodine, precedes the latter.

The author has made a series of determinations of the atomic weight of this element with very carefully purified material and believes he has been able to prove that the true atomic weight is less than that of iodine and therefore in agreement with the theory.

He calls attention to a complete summary of all the work on this question recently prepared by A. Gutbier,[2] and discusses the more important methods that have been used for determining the atomic weight of tellurium.

(*a*) The conversion of the metal into the oxide by the action of nitric acid. Brauner[3] ascribes the unsatisfactory results with this method to the fact that some of the oxides of nitrogen are retained until the temperature is reached at which the oxide begins to volatilize.

(*b*) By determining the bromine in the tetrabromide by titration, Brauner obtained concordant results, which were confirmed by Chikasige,[4] with an average value of 127.71.

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[1] Ber. d. chem. Ges., **40**, 4730 (1907).

[2] Sitzungsber. d. physik.-medizin. Soz. in Erlangen, **37**, 270 (1905).

[3] Monatsh. Chem., **10**, 411 (1898).

[4] J. Chem. Soc., **69**, 881.

(*c*) A number of investigators have used the method which depends upon the transformation of the dioxide into the metal. Staudenmaier,[1] using altogether, in two determinations, 3.5 grams, by reduction with hydrogen obtained an average of 127.57, which was also very closely approximated by Pellini. Heberlein obtained by this method the value 126.99 and Gutbier five results varying from 127.55 to 127.68. The latter investigator obtained almost the same results when the reduction took place in the wet way, using hydrazine as the reducing agent. Unfortunately, in no case where the dry method was used was the water, formed in the reduction, weighed.

(*d*) The basic nitrate method, depending upon the conversion of the compound $(TeO_2)_2HNO_3$ into the dioxide by heat. This method, first suggested by Norris, Fay and Edgerly,[2] may be open to the same criticism as the first method, the possibility that oxides of nitrogen are retained.

By this method, in a long series of experiments, Koethner obtained concordant results, recently confirmed by Norris, varying from 127.55 to 127.66. Gutbier obtained values varying from 125.8 to 127.8. One very strong objection to the use of this method is the great sensitiveness of the basic nitrate to moisture, which makes it necessary to remove the mother liquor with absolute alcohol.

(*e*) Telluric acid has also been used as the starting point in the determination of the atomic weights. Staudenmaier transformed the hydrate into the oxide and obtained an average result of 127.16. By reduction to the metal he obtained 127.28. Gutbier, using the same methods, but weighing the water formed, got 127.65 and 127.34. Heberlein found 126.72.

All experiments to show that the value as found was incorrect, owing to the presence of small amounts of a substance with a higher atomic weight, have failed.

The author separated 1500 grams of carefully purified telluric acid by several hundred crystallizations into twenty fractions and found no difference between the first and last fractions. Norris, Fay and Edgerly had carried out similar experiments with the compound K_2TeBr_6 with negative results. Having obtained the very pure telluric acid, the author determined the atomic weight of tellurium, using every precaution which was suggested by the results of the previous investigators. The material was first dried to constant weight in a vacuum desiccator over sulphuric acid. When this substance was heated the following reaction took place:

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[1] Z. anorg. Chem., **10**, 189.

[2] This Journal, **23**, 105.

$$H_6TeO_6 = TeO_2 + O + 3H_2O.$$

Instead of heating this material in a glass flask, as the previous investigators had done, the author used a platinum vessel and avoided errors in weighing by using as a counterpoise another vessel similar in every way. The vessel was heated by an electric stove, which heated only the bottom and thus allowed the upper part to remain cool and so condense any vapors of the oxide that might be formed. The temperature was raised very gradually, to prevent caking, until it reached 650° C. In some cases, in order to displace the oxygen from the vessel and to determine whether any of the material was lost as a volatile substance, a special cover was used which was so constructed that a current of dry air could be passed through the flask while the material was being heated. No evidence of loss was found.

In one case, No. 4, in the following table, the lower result is due to a very rapid heating, as the author conducted the experiment rapidly to determine when the decomposition was complete. The fractions used for the determinations were the first, ninth and twentieth. No. 4 was not included in the results:

No.	Fraction.	Weights of H_6TeO_6.	Weights of TeO_2.	Loss of weight (per cent).	Te.	Deviation from mean.
1	IX.	8.6277	5.9884	30.591	126.93	+0.08
2	I.	12.2680	8.5135	30.604	126.84	±0.01
3	I.	13.0051	9.0244	30.609	126.80	—0.05
4	XX.	8.6415	5.9947	30.629	126.65	......
5	XX.	8.4588	5.8696	30.6095	126.80	—0.05
6	XX.	8.0113	5.5599	30.591	126.94	+0.09
		50.3699	34.9558	30.602	126.85	

The experiments led to the unexpected result that the atomic weight of tellurium is Te = 126.85 ±0.02 (probable error), a value lower than iodine (126.97) and 0.75 unit less than the value considered most reliable by the International Commission. The author says it is very improbable that this method could introduce such an error and points out that not only do some of the earlier determinations approach very close to his, but that the determination of the carbon in diphenyl telluride, made by Steiner, give a value below 127, varying between 126.1 and 126.7. Brauner, as well as Gooch and

Peters, in a careful study of the composition of tellurium dioxide, point out that the results are always too high and the latter workers state that the results obtained would agree with the theoretical if tellurium had an atomic weight of 127 instead of 127.5. The author refers to the very disagreeable physiological results of working with these compounds.

J. E. G.

REVIEWS.

Annual Reports of the Progress of Chemistry for 1906. Issued by the Chemical Society. Vol. III. London: Gurney & Jackson. 1907.

This valuable publication of the London Chemical Society is made up of the sections below named: General and Physical Chemistry, by Alexander Findlay; Inorganic Chemistry, by P. Phillips Bedson; Organic Chemistry—Aliphatic Division, by H. J. H. Fenton; Organic Chemistry—Homocyclic Division, by Julius B. Cohen; Organic Chemistry—Heterocyclic Division, by John Theodore Hewitt; Stereochemistry, by William Jackson Pope; Analytical Chemistry, by Alfred Chaston Chapman; Physiological Chemistry, by W. D. Halliburton; Agricultural Chemistry and Vegetable Physiology, by John Augustus Voeleker; Mineralogical Chemistry, by Arthur Hutchinson; Radioactivity, by Frederick Soddy.

Each section is, in fact, a carefully prepared report presenting the results of investigations that appear to the author to be the most important of the year. It is therefore something like R. Meyer's Jahrbuch der Chemie, from which it differs in this respect, that it does not contain references to as many original articles while, in general, giving more space to the most important ones.

The object the writers have in view is thus stated by W. D. Halliburton, who prepared the report on Physiological Chemistry. He says: "I imagine further that it is not the object of such a report as this to epitomise still further the epitomes which have monthly made up the bulk of the Journal, but rather to give the writer * * an opportunity to enlarge upon certain aspects of the science with which he happens to be more familiar, and to exercise that right of comment which is denied to him when he merely presents an abstract."

A statement by Frederick Soddy, who prepared the report on Radioactivity, will be of general interest. It is this: "It may be stated without fear of contradiction that the theory that the atom is made up entirely or to any substantial extent of electrons is now generally regarded as being very much open to question. From spectroscopic and other evidence it is certain that electrons are universal constituents of atoms, but for the further very sweeping deduction that the atoms are composed of electrons there never has been much positive evidence in the past, while against the view some definite experimental evidence can now be urged."

POST'S CHEMISCH-TECHNISCHE ANALYSE. Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemischer Betriebe, für Handel und Unterricht. Dritte, veremhrte und verbesserte Auflage. Herausgegeben von PROFESSOR DR. BERNHARD NEUMANN. Erster Band, Drittes Heft. Braunschweig: Friedrich Vieweg u. Sohn. 1907. pp. 488–814. M. 7.

This section includes three chapters, those upon Iron, Nonferrous Metals and Salts of the Metals Other than the Alkalies and Alkaline Earths. The first is written by Professor A. Ledebur. This is in itself a guarantee that the results of long experience are incorporated in its pages and the methods selected are doubtless those which he has found reliable. The methods chosen represent essentially European practice and the American reader will again have occasion to wonder why it is that German authors so persistently avoid all reference to such convenient and useful procedures as the volumetric determination for phosphorus, in which the reduction of the molybdenum, by passing the solution through a column of powdered zinc, is substituted for the tedious solution of the zinc and the assumed reduction of the oxide MoO_3 to $Mo_{12}O_{19}$. The entire omission of any description of the determination of carbon by combustion in oxygen is also noteworthy, since this must still be regarded as a technical procedure which serves as a court of appeal when the results by other methods are questioned.

The subdivisions of the chapters are: Ores, Fluxes, Cast and Wrought Iron, Slags.

The second and third chapters are written by Professor B. Neumann, and include the analysis of sixteen of the more common metals, as well as tungsten, uranium, vanadium and molybdenum. The salts of ten of the common metals are discussed in the last chapter. The methods are selected from a wide range of authors and publications, and seem to indicate a thorough knowledge and good judgment in the choice of procedures. The high standard of the work, as a whole, is maintained in the section under review.

H. P. TALBOT.

POST'S CHEMISCH-TECHNISCHE ANALYSE: Handbuch der analytischen Untersuchungen zur Beaufsichtigung chemischer Betriebe, für Handel und Unterricht. Dritte, vermehrte und verbesserte Auflage. Herausgegeben von DR. BERNHARD NEUMANN. Zweiter Band, Zweites Heft. §§ 22–27. Braunschweig: Friedrich Vieweg und Sohn. 1907. Price, M. 10.

The fact that Section 22 (144 pp.) on the analytical methods used in the beet-sugar industry is an abridgment by Dr. Frühling of the sixth edition of his well-known work and that Section 26, on distilling (66 pp.), is largely taken by Dr. Hanow from the eighth edition of Märcker-Delbrück, bespeaks their excellence. Section 23 (72 pp.) on starch, dextrin and grape sugar is contributed by Dr. Parow, of the "Institut für Gärungsgewerbe und Stärkefabrikation." Section 24, on brewing (46 pp.), is by Drs. Vogel and Bleisch. Dr. Kulisch writes Section 25 on wine (90 pp.), and Dr. Rothenbach, also of the "Institut für Gärungsgewerbe," is responsible for Section 27, on vinegar, acetic acid and its compounds, and wood spirit (32 pp.).

The volume is characteristically German in that it ignores mention of all authorities not German and is consistently a compendium of German methods. Perhaps, when the index appears, in the due course of completion of the work, some references may be found to the classic method of the great English brewing chemists, Brown and Morris, for instance, or to some French analyst. The reviewer has failed to find but one reference to the work of a foreigner, and that on some trivial point of detail, among the host of authorities which are given.

The work is also characteristically German in the thoroughness of its editing and the excellence of its illustrations and typography.

GEO. W. ROLFE.

ELECTRO-ANALYSIS. By EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania. Fourth edition, revised and enlarged, with forty-two illustrations. Philadelphia: P. Blakiston's Son & Co. 1907. pp. 336. Price, $2.50 net.

The demand for this well-known and admirable laboratory guide, in this comparatively new field of quantitative analysis, is shown by the rapidity with which the first three editions were disposed of. In the preface to this, the fourth edition, the author states that "It appeared advisable to omit from this edition the several sections relating to the various sources of the current, particularly those in which the older forms of battery were described. * * *

The greater portion of the new material presented in the pages which follow refers to the rapid precipitation and separation of metals, the use of a mercury cathode with rotating anode, and the employment of a new cell in the determination of cations and anions."

The rapid growth of electro-analysis in the last decade or two is really due to the application of physical-chemical principles to the subject of quantitative analysis, and it would certainly make any analyst think, to hear the leading authority in this field in this country state, as he does in his preface, "that the estimation, for example, of barium and chlorine, in barium chloride, may be made in an hour or less."

It is not too much to say that the subject of analytical chemistry has, through electro-analysis, been fundamentally changed, if not, in part, actually revolutionized. We owe many of our best methods in this field to the author of this book.

The work of the printer also is admirably done, the book being well adapted in every respect to use in the laboratory. It will find, for a long time to come, a growing demand.

H. C. J.

IMMUNO-CHEMISTRY. The Application of the Principles of Physical Chemistry to the Study of the Biological Antibodies. By SVANTE ARRHENIUS. New York: The Macmillan Co. 1907. $1.60.

"Considering the very brief period during which physical-chemical methods have found application to the study of biological problems, the advance which has been made is very remarkable and there is every reason to believe that in the future, as the methods become more and more extensively applied, the advance will become more rapid and widespread."

These words of Al. Findlay could not have found a better verification than is afforded by this new book on immuno-chemistry by one of our greatest physical chemists.

The war between the two views concerning the nature of immuno-reactions has raged now for several years. Under such circumstances it seems of the greatest importance that the new ideas which Arrhenius has brought into this question are clearly set forth, not so much to convince the opponents as to allow the impartial reader to judge by himself as well as to interest new workers in this promising field.

It may be well to recall that for years Ehrlich has led the way in the study of the intricate questions concerning the toxins and antitoxins. To explain these phenomena he has built up a system almost as complicated as the structural formulae of organic chemistry. However, when Ehrlich tried to decide the question whether we are dealing here with chemical reactions or which physiological phenomena in the body, his "side chains" failed to give an answer and, moreover, failed to point to a method of experimental attack. Arrhenius, unencumbered by such hypotheses, has taken up this problem from the point of view of chemical equilibrium of incomplete reactions, to which the law of mass action must apply. To the physical chemist, who reads through the overwhelming mass of experimental evidence collected in this book, there can be no doubt that Arrhenius has attacked the problem in a way which from our present state of knowledge seems the best, if not the only one. Hence, as long as his opponents have not obtained quantitative results which contradict those of Arrhenius and his school, we may safely entrust ourselves to his guidance.

Since the book is of interest to medical men primarily, the special chapters are preceded by a geneal discussion of the reversibility of reactions, of velocity of reaction in homogeneous and heterogeneous systems, and of equilibria of absorption processes. One chapter each is devoted to the neutralization of diphtheria toxin, ricin, saponin and snake-venom, to the compound haemolysins and to the precipitins and their antibodies. The literature bearing on any of these questions has been considered most completely.

Although this new book is the outcome of a series of lectures delivered to the students at Berkeley, California, it makes considerable demand on the reader. This may be due to the fact that the subject is as yet quite unwieldly. At times, however, when the reasoning becomes quite involved and hard to follow, one feels the need of an Ostwald to make the difficult subject-matter more intelligible. Still a careful study of the book cannot be recommended too highly to every one interested in this question and to those who intend to keep pace with the rapid progress being made in the applications of physical chemistry to various phenomena.

GEORGE W. HEIMROD.

VORTRÄGE FÜR AERZTE ÜBER PHYSIKALISCHE CHEMIE. Von DR. ERNST COHEN. Zweite, vermehrte und verbesserte Auflage, mit 53 Figuren im Text. Leipzig: Verlag von Wilhelm Engelmann. 1907. pp. 264. M. 8; bound, M. 9.

The appearance of this book has already been referred to in THIS JOURNAL.[1] The early appearance of the second edition shows that it has met a want among physicians, who are now called upon, so frequently, to apply the fundamental principles of Physical Chemistry. It is fortunate that they have been supplied with a work from such a reliable and authoritative source, and equally fortunate that they have realized their opportunity and have used the book. H. C. J.

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[1] THIS JOURNAL, 30, 165.

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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 10°.[1]

BY H. N. MORSE AND H. V. MORSE.

In an earlier paper,[2] it was stated that the "considerable deviation of osmotic from gas pressure in the vicinity of 0°, while the two were found to be in substantial agreement in the neighborhood of 20°, made it desirable to determine the pressures of both cane sugar and glucose solutions at several intermediate temperatures;" and that "the intervals which have been selected for this purpose are 5°, 10° and 15°." The work upon cane sugar solutions at 5° has already been described.[3] The present paper gives an account of the pressures which they were found to exert at 10°.

The measurements in the present series are undoubtedly the most accurate which have thus far been made, owing to certain improvements in the method which have almost wholly eliminated the dilution of the solutions while in the cells.

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558 **38**, 175.

[2] THIS JOURNAL, **38**, 175.

[3] *Ibid.*, **38**, 175.

We have frequently referred[1] to this dilution of the cell contents—due, "*not to leakage*, but to the sucking in of water from the wall behind the membrane while the cell is being closed and opened"—as the most obstinate of all the large sources of error which have been encountered. In the case of cane sugar, the average loss in rotation while the solutions were in the cells was as follows: Series II,[2] 2.8 per cent; Series III,[3] 1.47 per cent; Series IV,[4] 1.28 per cent; while in the present series (V) there was loss in rotation in only eight of the twenty experiments. This loss, moreover, was in every instance small as compared with the pressures measured, as will be seen in the following tabular statement:

Pressure measured.	Correction for loss in rotation.
12.00 atmospheres	0.005 atmosphere.
17.09 "	0.005 "
19.73 "	0.025 "
22.22 "	0.06 "
24.97 "	0.09 "

The whole loss has been corrected as *inversion*, though a portion of it is undoubtedly due to dilution. The quantities in question are, however, so small that they do not materially affect the results, whether the whole error is ascribed, on the one hand, to inversion, or, on the other, to dilution; or a part to inversion, and the remainder to dilution.

It is also to be noted that the temperatures maintained in the present work are much more constant than in any former series of measurements.

The material employed was from the same supply as that used in former measurements, and the statements made in earlier papers regarding its purity need not be repeated.

It may be noticed that the rotation of solutions of equal weight-normal concentration are not always identical. This is due to differences in the temperatures at which the rotation was determined.

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[1] THIS JOURNAL, **36**, 26 and 49; **37**, 325; **37**, 327; **38**, 178.

[2] *Ibid.*, **36**, 39.

[3] *Ibid.*, **37**, 457.

[4] *Ibid.*, **38**, 175.

Table I.

0.1 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 12°.8; (2) at conclusion of experiment, 12°.8; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.08 mm. Cell used, H. Resistance of membrane, 136,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.46; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.97. Time of setting up cell, 4 P.M., March 2, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
March 5.						
11.45 P.M.	10°.0	10°.9	147.12	2.42	2.31	0.11
March 6.						
10.30 A.M.	10°.0	10°.7	146.78	2.43	2.31	0.12
				2.43	2.31	0.12

Molecular osmotic pressure, 24.25.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.050.

Table II.

0.1 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 12°.8; (2) at conclusion of experiment, 12°.8; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 219,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.69. Time of setting up cell, 3.30 P.M., March 2, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
March 5.						
8.40 A.M.	10°.0	10°.3	136.68	2.43	2.31	0.12
11.15 P.M.	10°.0	10°.9	136.17	2.45	2.31	0.14
March 6.						
10.30 A.M.	10°.0	10°.7	136.28	2.44	2.31	0.13
				2.44	2.31	0.13

Molecular osmotic pressure, 24.40.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.056.

Table III.

0.2 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 25°.0; (2) at conclusion of experiment, 25°.0; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 283,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.56; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02 Initial pressure, 4.66. Time of setting up cell, 11.30 A.M., January 21, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Jan. 22.						
11.40 A.M.	10°.2	10°.8	82.91	4.80	4.62	0.18
8.10 P.M.	10°.0	10°.9	82.87	4.80	4.62	0.18
Jan. 23.						
10.00 A.M.	10°.0	10°.7	82.37	4.83	4.62	0.21
				4.81	4.62	0.19

Molecular osmotic pressure, 24.05.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.041.

Table IV.

0.2 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 25°.0; (2) at conclusion of experiment, 25°.0; loss, 0°. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.14 mm. Cell used, D. Resistance of membrane, 141,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.78. Time of setting up cell, 11.30 A.M., January 21, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Jan. 22.						
11.40 A.M.	10°.2	10°.8	76.98	4.82	4.62	0.20
8.10 P.M.	10°.0	10°.9	76.98	4.82	4.62	0.20
10.30 P.M.	10°.0	10°.8	76.84	4.83	4.62	0.21
Jan. 23.						
10.00 A.M.	10°.0	10°.7	76.62	4.85	4.62	0.23
				4.83	4.62	0.21

Molecular osmotic pressure, 24.15.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.045.

Table V.

0.3 wt. normal solution, Experiment No. 1. *Rotation:* (1) original, 36°.6; (2) at conclusion of experiment, 36°.6; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.02 mm. Cell used, G. Resistance of membrane, 158,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.00. Time of setting up cell, 5.00 P.M., March 12, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 13.						
10.30 P.M.	10°.0	10°.6	53.40	7.20	6.92	0.28
March 14.						
8.45 P.M.	10°.0	10°.7	53.16	7.24	6.92	0.32
March 15.						
10.00 A.M.	10°.0	10°.8	53.44	7.21	6.92	0.29
				7.22	6.92	0.30

Molecular osmotic pressure, 24.07.
Molecular gas pressure, 23.07.
Ratio of osmotic to gas pressure, 1.043.

Table VI.

0.3 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 36°.7; (2) at conclusion of experiment, 36°.7; loss, 0.°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.08 mm. Cell used, O. Resistance of membrane, 112,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.36. Time of setting up cell, 4.00 P.M., March 17; 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 19.						
5.00 P.M.	10°.00	10°.9	53.79	7.15	6.92	0.23
10.00 P.M.	10°.10	10°.9	53.86	7.14	6.93	0.21
March 20.						
8.30 A.M.	10°.10	10°.6	53.65	7.17	6.93	0.24
10.30 P.M.	10°.00	10°.8	53.73	7.15	6.92	0.23
				7.15	6.93	0.22

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.032.

Table VII.

0.4 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 48°.1; (2) at conclusion of experiment, 48°.1; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.0 mm. Cell used, H. Resistance of membrane, 183,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.61. Time of setting up cell, 4 P.M., February 24, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 25.						
8.00 P.M.	10°.1	11°.2	40.86	9.53	9.24	0.29
Feb. 26.						
8.00 P.M.	10°.1	10°.6	40.98	9.52	9.24	0.28
10.00 P.M.	10°.0	10°.9	40.85	9.54	9.23	0.31
				9.53	9.24	0.29

Molecular osmotic pressure, 23.83.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.031.

Table VIII.

0.4 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 48°.1; (2) at conclusion of experiment, 48°.1; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.14 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.55. Time of setting up cell, 4.30 P.M., February 24, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 25.						
8.30 A.M.	10°.1	10.75	43.17	9.64	9.24	0.40
2.00 P.M.	10°.1	10.9	43.37	9.59	9.24	0.35
5.00 P.M.	10°.05	11.0	43.34	9.61	9.23	0.38
Feb. 26.						
10.00 P.M.	10°.00	10.9	43.38	9.61	9.23	0.38
				9.61	9.24	0.38

Molecular osmotic pressure, 24.03.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.040.

Table IX.

0.5 wt. normal solution. Experiment No. 1. *Rotatation:* (1) original, 59°.00; (2) at conclusion of experiment, 59°.00; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.03 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.9. Time of setting up cell, 3.30 P.M., February 20, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
Feb. 21.						
9.00 A.M.	10°.0	10°.6	35.13	11.95	11.54	0.41
5.00 P.M.	10°.0	11°.0	35.11	11.96	11.54	0.42
Feb. 22.						
9.00 A.M.	10°.0	10°.4	35.15	11.94	11.54	0.40
4.00 P.M.	9°.9	10°.8	35.04	11.98	11.54	0.44
				11.96	11.54	0.42

Molecular osmotic pressure, 23.92.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.036.

Table X.

0.5 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 58°.7; (2) at conclusion of experiment, 58°.6; loss, 0°.1 = 0.17 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.64 mm. Cell used, G. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 3.88. Time of setting up cell, 4.00 P.M., March 17, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
March 18.						
10.00 P.M.	10°.0	10°.9	35.00	12.00	11.54	0.46
March 19.						
8.00 P.M.	10°.0	10°.8	34.87	12.04	11.54	0.50
March 20.						
10.30 A.M.	10°.0	10°.8	34.89	12.00	11.54	0.50
				12.01	11.54	0.49

Molecular osmotic pressure, 24.02.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.040.

Table XI.

0.6 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 69°.2; (2) at conclusion of experiment, 69°.2. loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.06 mm. Cell used, D. Resistance of membrane, 185,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.57. Time of setting up cell, 5.00 P.M., February 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 18.						
9.00 A.M.	10°.1	10°.4	29.10	14.50	13.85	0.65
5.00 P.M.	10°.1	10°.8	29.02	14.55	13.85	0.70
Feb. 19.						
2.00 P.M.	10°.1	10°.4	29.11	14.53	13.85	0.68
				14.53	13.85	0.68

Molecular osmotic pressure, 24.22.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.049.

Table XII.

0.6 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 69°.2; (2) at conclusion of experiment, 69°.2; loss, 0°. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.03 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.8. Time of setting up cell, 5.00 P.M., February 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solution.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Feb. 18.						
9.00 A.M.	10°.1	10°.4	27.19	14.53	13.85	0.68
5.00 P.M.	10°.1	10°.8	27.11	14.57	13.85	0.72
Feb. 19.						
9.00 A.M.	10°.1	10°.5	27.20	14.53	13.85	0.68
2.00 P.M.	10°.1	10°.4	27.17	14.57	13.85	0.72
				14.55	13.85	0.70

Molecular osmotic pressure, 24.25.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.051.

Table XIII.

0.7 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 79°.3; (2) at conclusion of experiment, 79°.2; loss, 0°.1 = 0.13 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.16 mm. Cell used, G. Resistance of membrane, 373,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.38. Time of setting up cell, 4.00 P.M., January 24, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 25.						
11.00 A.M.	10°.1	10°.4	23.19	17.10	16.16	0.94
2.00 P.M.	10°.0	10°.7	23.18	17.11	16.16	0.95
5.00 P.M.	10°.0	10°.8	23.23	17.07	16.16	0.91
				17.09	16.16	0.93

Molecular osmotic pressure, 24.41.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.058.

Table XIV.

0.7 wt. normal solution. Experiment No 2. *Rotation:* (1) original, 79°.3; (2) at conclusion of experiment, 79°.3; loss, 0°. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.17 mm. Cell used, D. Resistance of membrane, 187,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.63; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.93. Time of setting up cell, 4.00 P.M., January 24, 1908.

Time.	Temperature.		Volume N_2.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 25.						
11.00 A.M.	10°.1	10°.4	24.85	17.07	16.16	0.91
2.00 P.M.	10°.0	10°.7	24.84	17.08	16.16	0.92
5.00 P.M.	10°.0	10°.8	24.82	17.10	16.16	0.94
				17.08	16.16	0.92

Molecular osmotic pressure, 24.40.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.057.

Table XV.

0.8 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 89°.1; (2) at conclusion of experiment, 88°.9; loss, 0°.2 = 0.22 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.28 mm. Cell used, G. Resistance of membrane, 186,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.62; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.96. Time of setting up cell, 5.00 P.M., January 29, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
Jan. 30.						
9.00 P.M.	9°.9	10°.8	20.17	19.70	18.46	1.24
Jan. 31.						
2.00 P.M.	10°.0	10°.6	20.14	19.73	18.47	1.26
4.00 P.M.	10°.0	10°.7	20.19	19.68	18.47	1.21
				19.70	18.47	1.23

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.63.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 89°.1; at conclusion of experiment, 89°.0; loss, 0°.1 = 0.11 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.25 mm. Cell used, D. Resistance of membrane, 184,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.64; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.46. Time of setting up cell, 5.00 P.M., January 29, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
Jan. 30.						
2.00 P.M.	10°.0	10°.6	21.49	19.77	18.47	1.30
Jan. 31.						
2.00 P.M.	10°.0	10°.6	21.52	19.74	18.47	1.27
4.00 P.M.	10°.0	10°.7	21.52	19.75	18.47	1.28
				19.75	18.47	1.28

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.69.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.069.

Table XVII.

0.9 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 98°.4; (2) at conclusion of experiment, 98°.0; loss, 0°.4 = 0.41 per cent. *Manometer:* No. 6; volume of nitrogen, 405.34; displacement, 0.88 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.62; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.94. Time of setting up cell, 4.00 P.M., February 14, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
Feb. 15.						
1.00 P.M.	10°.0	11°.4	17.91	22.24	20.77	1.47
11.00 P.M.	10°.0	10°.6	17.93	22.22	20.77	1.45
Feb. 16.						
10.00 A.M.	10°.0	10°.4	17.93	22.20	20.77	1.43
				22.22	20.77	1.45

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.69.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.070.

Table XVIII.

0.9 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 98°.4; (2) at conclusion of experiment, 98°.0; loss, 0°.4 = 0.41 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 0.68 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections:* (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.64; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.33. Time of setting up cell, 4.00 P.M., February 14, 1908.

	Temperature.			Pressure.		
Time.	Solution.	Manometer.	Volume N_2.	Osmotic.	Gas.	Difference.
Feb. 15.						
11.30 P.M.	10°.0	10°.6	19.18	22.22	20.77	1.45
Feb. 16.						
10.00 A.M.	10°.0	10°.4	19.15	22.21	20.77	1.44
				22.22	20.77	1.45

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.69.
Molecular gas pressure, 23.08.
Ratio of osmotic to gas pressure, 1.070.

Table XIX.

1.0 wt. normal solution. Experiment No. 1. *Rotation:* (1) original, 107°.4; (2) at conclusion of experiment, 106°.8; loss, 0°.6 = 0.56 per cent. *Manometer:* No. 13; volume of nitrogen, 432.84; displacement, 1.29 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.64; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.89. Time of setting up cell, 5.00 P.M., February 11, 1908.

Time.	Temperature. Solution.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Feb. 12.						
8.00 P.M.	10°.3	11°.6	17.04	24.95	23.11	1.84
Feb. 13.						
9.00 A.M.	10°.2	10°.5	17.00	25.03	23.10	1.93
2.00 P.M.	10°.0	10°.9	17.03	24.98	23.08	1.90
				24.99	23.10	1.89

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.99.
Molecular gas pressure, 23.10.
Ratio of osmotic to gas pressure, 1.081.

Table XX.

1.0 wt. normal solution. Experiment No. 2. *Rotation:* (1) original, 107°.4; (2) at conclusion of experiment, 106°.8; loss, 0°.6 = 0.56 per cent. *Manometer:* No. 8; volume of nitrogen, 473.36; displacement, 0.85 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.66; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.24. Time of setting up cell, 5.00 P.M., February 11, 1908.

Time.	Temperature. Solution.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Feb. 12.						
11.30 P.M.	10°.2	10°.4	18.67	24.94	23.10	1.84
Feb. 13.						
9.00 A.M.	10°.2	10°.5	18.66	24.95	23.10	1.85
2.00 P.M.	10°.0	10°.9	18.68	24.92	23.08	1.84
				24.94	23.09	1.85

Loss in rotation corrected as inversion.
Molecular osmotic pressure, 24.94.
Molecular gas pressure, 23.09.
Ratio of osmotic to gas pressure, 1.080.

Table XXI.—Summary of Results.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	10°.0	0°.0	0.00	2.43	2.31	0.12	24.25	23.10	1.050
0.1	10°.0	0°.0	0.00	2.44	2.31	0.13	24.40	23.10	1.056
0.2	10°.0	0°.0	0.00	4.81	4.62	0.19	24.05	23.10	1.041
0.2	10°.0	0°.0	0.00	4.83	4.62	0.21	24.15	23.10	1.045
0.3	10°.0	0°.0	0.00	7.22	6.92	0.30	24.07	23.07	1.043
0.3	10°.1	0°.0	0.00	7.15	6.93	0.22	23.83	23.08	1.032
0.4	10°.1	0°.0	0.00	9.53	9.24	0.29	23.83	23.10	1.031
0.4	10°.1	0°.0	0.00	9.61	9.24	0.37	24.03	23.10	1.040
0.5	10°.0	0°.0	0.00	11.96	11.54	0.42	23.92	23.08	1.036
0.5	10°.0	0°.1	0.01	12.01	11.54	0.49	24.01	23.09	1.042
0.6	10°.1	0°.0	0.00	14.53	13.85	0.68	24.22	23.09	1.049
0.6	10°.1	0°.0	0.00	14.55	13.85	0.70	24.25	23.09	1.051
0.7	10°.0	0°.1	0.01	17.09	16.16	0.93	24.41	23.09	1.058
0.7	10°.0	0°.0	0.00	17.08	16.16	0.92	24.40	23.09	1.057
0.8	10°.0	0°.2	0.03	19.70	18.47	1.23	24.63	23.09	1.067
0.8	10°.0	0°.1	0.02	19.75	18.47	1.28	24.69	23.09	1.069
0.9	10°.0	0°.4	0.06	22.22	20.77	1.45	24.69	23.08	1.070
0.9	10°.0	0°.4	0.06	22.22	20.77	1.45	24.69	23.08	1.070
1.0	10°.1	0°.6	0.09	24.99	23.10	1.89	24.99	23.10	1.081
1.0	10°.1	0°.6	0.09	24.94	23.08	1.85	24.94	23.09	1.080

Table XXII.—Summary of Results. Mean Values.

Concentration.	Temperature.	Loss in rotation.	Correction for inversion.	Osmotic pressure.	Gas pressure	Difference.
0.1	10°.0	0°.0	0.0	2.44	2.31	0.13
0.2	10°.0	0°.0	0.0	4.82	4.62	0.20
0.3	10°.1	0°.0	0.0	7.19	6.93	0.26
0.4	10°.1	0°.0	0.0	9.57	9.24	0.33
0.5	10°.0	0°.05	0.005	12.00	11.54	0.46
0.6	10°.0	0°.00	0.00	14.54	13.85	0.69
0.7	10°.0	0°.05	0.005	17.09	16.16	0.93
0.8	10°.0	0°.15	0.025	19.73	18.47	1.26
0.9	10°.0	0°.40	0.06	22.22	20.77	1.45
1.0	10°.1	0°.60	0.09	24.97	23.09	1.87

Table XXII.—(Continued).

Concentration.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	24.33	23.10	1.053
0.2	24.10	23.10	1.043
0.3	23.95	23.08	1.038
0.4	23.93	23.10	1.036
0.5	23.97	23.09	1.039
0.6	24.24	23.09	1.050
0.7	24.41	23.09	1.058
0.8	24.66	23.09	1.068
0.9	24.69	23.08	1.070
1.0	24.97	23.10	1.081

It will be seen from Tables XXI. and XXII., which contain summaries of the results at 10°, that, at this temperature, the osmotic pressure of cane sugar solutions exhibits the same peculiarities that were observed at 0° and 5°, that is, an osmotic pressure which considerably exceeds the calculated gas pressure, and which diminishes slightly (relatively) from the 0.1 to the 0.4 weight-normal solution, and then increases with increasing concentration. If the pressures at 0°, 5° and 10° are compared, there is some evidence of a temperature coefficient to be discovered. This fact will be further commented upon when we present the results obtained at 15°.

Johns Hopkins University,
March 30, 1908.

[Contribution from the Chemical Laboratory of the University of Michigan.]

ON THE CONDENSATION OF NITROMALONIC ALDEHYDE WITH ACETONYLACETONE.

[FIRST PAPER.]

By William J. Hale and Charles A. Robertson.

In previous communications by Hill, Torrey, and others,[1] the work upon the condensation of nitromalonic aldehyde with acetone and its derivatives has been carefully described. The general mode of condensation has been found to be uniform throughout and has always yielded the expected benzol derivatives, the constitution of which depended upon the substituents in the acetone molecule. The extension of this work to the diketones has seemed to us desirable. We have, accordingly, selected, in the first place, that ketone which would present two acetone nuclei, namely, acetonylacetone. In accordance with results from the earlier work (*loc. cit.*) we should expect to obtain from the condensation of this diketone with 2 molecules of nitromalonic aldehyde a dinitrodioxydiphenyl. In a contribution by Hill and one of us,[1] "On the Condensation of Nitromalonic Aldehyde with Benzylmethyl Ketone," it was shown that the production of a diphenyl derivative was attended with no difficulty whatsoever. We were led, therefore, to infer that in the condensation of 2 molecules of nitromalonic aldehyde with 1 molecule of acetonylacetone, a derivative of benzylmethyl ketone might possibly be first formed, but that as the result of a subsequent and final condensation this latter compound and the second molecule of nitromalonic aldehyde present would give the expected diphenyl derivative.

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[1] This Journal, **22**, 89 (1899); **24**, 1 (1900).

Into a reaction mixture containing two molecules of nitromalonic aldehyde and one of acetonylacetone, together with sodium hydroxide as a condensing agent, a current of carbon dioxide was passed in order to precipitate any of the nitrophenol that might in this way have been formed. A small amount of a yellow substance was readily thrown down. Its examinations clearly showed that we had to deal with a derivative of benzylmethyl ketone, a 2-acetonyl-4-nitrophenol, and that the condensation, therefore, had been, to a slight extent, at least, arrested at its middle stage. From the mother liquors, by acidification with hydrochloric acid, a large quantity of a light, yellow, crystalline substance was obtained. An examination proved that this was not the dinitrodioxydiphenyl we had anticipated, but a compound of an entirely different constitution. As it is the result of a new condensation, its description and study will be reserved for a second paper. From the facts just stated, we conclude that the first stage in this condensation must consist in the union of one molecule of nitromalonic aldehyde with one molecule of acetonylacetone to give a 1-nitro-3-acetonyl-4-keto-Δ-2,5-dihydro-benzol, which passes over at once, upon acidification, into the 2-acetonyl-4-nitrophenol. Experiments have shown that the second molecule of nitromalonic aldehyde, under the conditions to be described later, does not enter into the reaction, and the same quantity of acetonyl-nitrophenol, as well of the light-yellow product from the mother liquor, may be obtained from the use of but one molecule of the aldehyde. We have then to deal with the simple reaction between one molecule of the aldehyde and one molecule of ketone:

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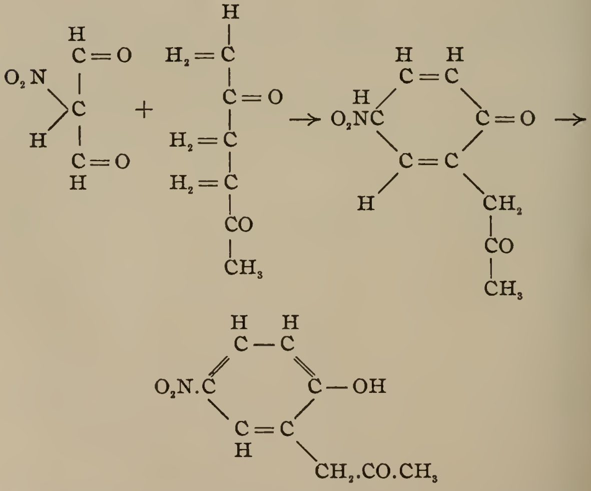
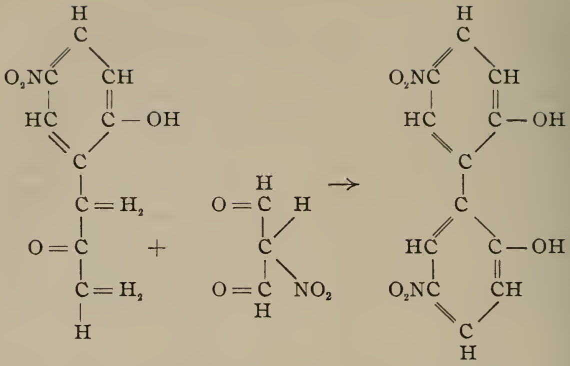
[1] THIS JOURNAL, **33**, 1 (1905).



The absence of any derivative of diphenyl in the reaction mixture is strongly indicative of the retarding influence which the substituent groups in the phenyl ring of the acetonyl-nitrophenol exert upon the further condensation between aldehyde and ketone.

Acetonylnitrophenol is a colorless, crystalline compound when pure. The sodium salt crystallizes in orange-red prisms changing to deep crimson upon dehydration. The action of alkyl haloids upon the sodium salts served as a method for obtaining the monoalkyl ethers of the compound and also for establishing the presence of but one hydroxyl group. The presence of the free ketone group in the acetonyl side chain is easily confirmed by the formation of an oxime. Oxidation of the methyl ether of this phenol by means of chromic acid gives the methyl ether of 5-nitrosalicylic acid and establishes, therefore, the constitution assigned. The compound undergoes nitration with ease, giving a 2-acetonyl-4,6-dinitrophenol with properties quite similar to the original mononitroderivative. The presence of an acetonyl group as a side chain in this compound leads at once to the inference that a second condensation with a molecule of nitromalonic aldehyde is possible under the proper conditions. To overcome the strongly negative character of the nitrophenolic group, its conversion into the form of an alkyl ether was found to suffice. The variation in the chemical constitution between a free phenol and its alkyl ether on the one hand, and that of its metallic salt on the other, may offer an explanation for the change in character of the phenyl group under these conditions. When the ethyl ether of acetonylnitrophenol condenses with one molecule of nitromalonic aldehyde in slightly alkaline solution, the reaction runs quite smoothly to the formation of a monoethyl ether of dinitrodioxydiphenyl, which can be easily precipitated with hydrochloric acid. In order to make possible the condensation of the free substance—the 2-acetonyl-4-nitrophenol—with one molecule of nitromalonic aldehyde, it was found necessary to alter the general method in use, by the employment of a large excess of alkali as the condensing agent. The excess of alkali may be considered to drive back the dissociation of the hydroxyl group and thus to lessen the strongly negative character of the entire phenyl ring.

[1] Baly, Edwards, and Stewart: J. Chem. Soc., **89**, 514 (1906).



In this case a derivative of a phenyldihydrobenzol may be regarded as the intermediate product, but upon acidification it passes rapidly into a 3,3′-dinitro-6,6′-dioxydiphenyl. A few of the derivatives of the several condensation products, sufficient to establish the constitution of all the compounds concerned and to indicate the general nature of these condensations, will be described.

EXPERIMENTAL PART.

Acetonylacetone was prepared by the method of Knorr,[1] and sodium nitromalonic aldehyde according to the directions of Hill and Torrey.[2]

2-Acetonyl-4-nitrophenol, $(CH_3.CO.CH_2)C_6H_3(NO_2)(OH)$.—One molecule of sodium nitromalonic aldehyde and slightly more than 1 molecule of acetonylacetone ($1^1/$ molecules are found quite sufficient) are dissolved in water with the addition of $^1/_8$ molecule of sodium hydroxide. The strength of the alkaline solution should not exceed N/10, and the temperature of the mixture should not be allowed to rise over that of a low room-temperature. The slight excess of acetonylacetone insures the complete combination of all the aldehyde with the ketone and thus prevents any possibility of the formation of trinitrobenzol upon acidification of the reaction mixture, a possible result in the acidification of sodium nitromalonic aldehyde.[1] The amount of the alkali used is small, owing to the tendency for the second condensation already mentioned to take place. The presence of less than $^1/_8$ molecule of sodium hydroxide has been found not only to retard the progress of condensation but also to interfere materially with the precipitation of the free acetonylnitrophenol by carbon dioxide, other condensation products being simultaneously precipitated. In practice, 8 grams of sodium nitromalonic aldehyde are dissolved in 100 cc. of water, and to this solution 6.8 grams of acetonylacetone and 0.2 gram of sodium hydroxide are added. The color of the liquid soon becomes a deep red and after the lapse of 48 hours the condensation may be assumed to be complete. The solution is now diluted with water to twice its volume, in order to prevent a separation of the sodium salts of the products formed, and then treated with a rapid current of carbon dioxide to the point of saturation, when all of the acetonylnitrophenol will be precipitated in small, light-yellow crystals. The yield, however, is very poor, 1.7 grams, amounting to not more than 17 per cent of the theoretical quantity. This low yield is due, of course, to the formation of the new product now under investigation, about 65 per cent of the theoretical quantity being formed under the above conditions. The relative amounts of this new substance and of the acetonylnitrophenol remain practically the same under most conditions, approximating a ratio of 4:1 and changing only when the conditions are such as to involve the acetonylnitrophenol in secondary reactions. The use of piperidine as a condensing agent has been found to give good results. The same proportions and degree of dilutions as in the previous method are employed, excepting that a few drops of piperidine replace the sodium hydroxide. In a very short time the solution takes on a red color and gives after 48 hours about the same relative amounts of condensation products as in the former case. The crude product is most conveniently purified by several crystallizations from glacial acetic acid. 2-Acetonyl-4-nitrophenol is readily soluble in acetone; fairly soluble in carbon disulphide, hot alcohol, or hot chloroform; from the two latter it may be crystallized. It is only sparingly soluble in benzol or carbon tetrachloride, and insoluble in ether, ligroin, or water, though boiling water dissolves it to a slight extent and deposits it again upon cooling in long, slender needles. From its solution in hot glacial acetic acid it crystallizes in beautiful, thin, colorless prisms which melt at 188.5° (corr.).

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[1] Ber. d. chem. Ges., **22**, 2100 (1889).

[2] THIS JOURNAL, **22**, 25 (1899).

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[1] This Journal, **22**, 98 (1899).

I. 0.1600 gram substance gave 0.3242 gram CO_2 and 0.0702 gram H_2O.

II. 0.2048 gram substance gave 13.7 cc. moist N at 20° and 734 mm. pressure.

	Calculated for $C_9H_9O_4N$.	Found. I.	II.
C	55.42	55.27	...
H	4.65	4.90	...
N	7.20	...	7.35

The Sodium Salt of 2-Acetonyl-4-nitrophenol.—When the free phenol is dissolved in water with just sufficient sodium hydroxide to effect neutralization, the sodium salt of the acetonylnitrophenol will separate, upon sufficient concentration, in small hexagonal plates of a bright-yellow color. This salt crystallizes well with 2 molecules of water of crystallization. A great part of this water of crystallization is lost over sulphuric acid, but the dehydration is not complete till 125°, the salt in the meantime having passed from a bright-yellow to the dark-red color of the anhydrous salt.

I. 0.6750 gram air-dried salt lost, at 125°, 0.0958 gram H_2O.

II. 0.1960 gram air-dried salt gave 0.0552 gram Na_2SO_4.

	Calculated for $C_9H_8O_4NNa.2H_2O$.	Found. I.	II.
H_2O	14.22	14.19	...
Na	9.10	...	9.13

2-Acetonyl-4-nitrophenol Methyl Ether, $(CH_3.CO.CH_2)C_6H_3(NO_2)(OCH_3)$.—The methyl ether is readily prepared by the action of methyl iodide upon the sodium salt of the acetonylnitrophenol in alcoholic solution. After several hours' boiling on the water bath, under a reflux condenser, the clear solution is evaporated to dryness and the mass extracted with ether. Upon recrystallization from ether by the addition of low-boiling ligroin, the pure product melting at 60° (corr.) was obtained. The methyl ether is readily soluble in benzol, ether, acetone, chloroform, carbon tetrachloride, or alcohol; fairly soluble in hot ligroin, and insoluble in water. It is but sparingly soluble in low-boiling ligroin.

I. 0.1196 gram substance gave 0.2510 gram CO_2 and 0.0580 gram H_2O.

II. 0.2687 gram substance gave 17.2 cc. moist N at 23.6° and 735.4 mm. pressure.

	Calculated for $C_{10}H_{11}O_4N$.	Found. I.	II.
C	57.40	57.24	...
H	5.30	5.42	...
N	6.71	...	6.92

2-Acetonyl-4-nitrophenol Ethyl Ether, $(CH_3.CO.CH_2)C_6H_3(NO_2)(OC_2H_5)$.—The ethyl ether may be prepared by the action of ethyl iodide upon the sodium salt in a manner exactly similar to the preparation of the methyl ether. The solubilities of the ethyl ether are, in almost all respects, identical with those of the methyl ether, except that it is less markedly soluble in low-boiling ligroin. From its solution in ether, colorless prisms separate upon the addition of ligroin. They have a melting point of 70.5° (corr.).

I. 0.1456 gram substance gave 0.3150 gram CO_2 and 0.0794 gram H_2O.

II. 0.2478 gram substance gave 14.5 cc. moist N at 22° and 738 mm. pressure.

	Calculated for $C_{11}H_{13}O_4N$.	Found. I.	II.
C	59.16	59.00	...
H	5.87	6.10	...
N	6.29	...	6.40

Oxidation of 2-Acetonyl-4-nitrophenol Methyl Ether.—In order to establish conclusively the relative position of the acetonyl group in acetonylnitrophenol, the oxidation of the methyl ether was attempted. Two grams of methyl ether were treated with a 4 per cent solution of potassium permanganate containing slightly more than the calculated quantity (5 molecules) of the salt. After 5-10 minutes' boiling, the excess of permanganate was decomposed by the addition of a few drops of alcohol, and the manganese dioxide filtered off. The clear filtrate was now acidified with hydrochloric acid and extracted with ether. The ether extract yielded a white product which melted at 148°-150°. This product showed all the properties of 5-nitrosalicylic acid methyl ether (m. p. 148°-149°). The result, therefore, establishes the constitution already assigned, by showing the acetonyl group is in the ortho position to the hydroxyl group in the original compound.

Oxime of 2-Acetonyl-4-nitrophenol Ethyl Ether, $(CH_3.C:NOH.CH_2)C_6H_3(NO_2)(OC_2H_5)$.—The oxime may be easily prepared by adding an alcoholic solution of acetonylnitrophenol ethyl ether to a concentrated aqueous solution of hydroxylamine hydrochlorate neutralized with a potassium carbonate solution. The oxime is precipitated in a short time. The product crystallizes out of alcohol in beautiful, colorless needles melting at 146° (corr.). It is extremely soluble in acetone, ethyl acetate, or chloroform; fairly soluble in hot benzol or alcohol, and nearly insoluble in ligroin or water. The formation of the oxime confirms the presence of the carbonyl, and hence the acetonyl, group in the original compound.

I. 0.1148 gram substance gave 0.2326 gram CO_2 and 0.0626 gram H_2O.

II. 0.1692 gram substance gave 18.4 cc. moist N at 23.5° and 748 mm. pressure.

	Calculated for $C_{11}H_{14}O_4N_2$.	Found. I.	II.
C	55.43	55.27	...
H	5.91	6.12	...
N	11.79	...	11.97

2-Acetonyl-4,6-dinitrophenol, $(CH_3.CO.CH_2)C_6H_2(NO_2)_2(OH)$.—Two grams of acetonylnitrophenol were dissolved in 40 grams glacial acetic acid with the aid of gentle warming. Four grams of nitric acid (sp. gr. 1.40) were now added and the gentle warming continued for a few minutes only. The clear liquid must be cooled quickly and diluted with an equal volume of water, when the crystalline plates of the acetonyldinitrophenol soon make their appearance. This product may be easily crystallized out of glacial acetic acid, in which, however, it is quite soluble even in the cold. It is readily soluble in hot benzol or hot alcohol, in chloroform, acetone, or ethyl acetate; it is fairly soluble in ether or carbon disulphide, and but sparingly soluble in ligroin. In water it is slightly more soluble than the mononitro derivative. From its solution in hot benzol, beautiful glistening laminae which melt at 121° (corr.) separate upon the addition of ligroin.

I. 0.1098 gram substance gave 0.1803 gram CO_2 and 0.0368 gram H_2O.

II. 0.1602 gram substance gave 17.4 cc. moist N at 24.5° and 742 mm. pressure.

	Calculated for $C_9H_8N_2O_6$.	Found. I.	Found. II.
C	44.96	44.77	...
H	3.35	3.75	...
N	11.69	...	11.80

2-Acetonyl-4,6-dinitrophenol Ethyl Ether, $(CH_3.CO.CH_2)C_6H_2(NO_2)_2(OC_2H_5)$.—The sodium salt of 2-acetonyl-4,6-dinitrophenol may be prepared in a manner exactly analogous to that for the sodium salt of the mononitrophenol, to which this salt bears also a close resemblance. The dried sodium salt is treated with ethyl iodide, using ethyl alcohol as a diluent and solvent, in the same manner as described for the preparation of an ether of the mononitro derivative. The ether extract gives a good yield of the product. This may be purified by crystallization from ligroin from which it separates in small, colorless prisms melting at 118.5° (corr.). The ethyl ether of acetonyldinitrophenol is readily soluble in acetone or ethyl acetate; fairly soluble in chloroform, benzol, or ether; and insoluble in ligroin and water.

I. 0.1304 gram substance gave 0.2348 gram CO_2 and 0.0564 gram H_2O.

II. 0.1600 gram substance gave 15.5 cc. moist N at 20.5° and 732.4 mm. pressure.

	Calculated for $C_{11}H_{12}O_6N_2$.	Found. I.	II.
C	49.22	49.12	...
H	4.51	4.84	...
N	10.47	...	10.59

3,3′-Dinitro-6,6′-dioxydiphenyl,
$(HO)(NO_2)C_6H_3.C_6H_3(NO_2)(OH)$.—The presence of the acetonyl group in the compounds just described indicated at once the possibility of further condensation with nitromalonic aldehyde. As has already been mentioned, the presence of a second molecule of nitromalonic aldehyde in the preparation of acetonylnitrophenol did not in itself afford the condition for this further condensation. The use, however, of a large excess of alkali was found to have the desired effect, and under its influence, acetonylnitrophenol readily underwent the second condensation with the aldehyde. Two grams (1 molecule) of acetonylnitrophenol, together with 1.7 grams (slightly more than 1 molecule) of sodium nitromalonic aldehyde, were brought into solution in 40 cc. of water with the aid of 2 grams (5 molecules) of sodium hydroxide, giving an exactly normal solution of free alkali, *i. e.*, in excess of that required for neutralization. After standing 2 to 3 days at room temperatures, the liquid, in which a deep red color had developed, was diluted with 200 to 300 cc. of water and treated with a current of carbon dioxide. As no appreciable precipitate was formed, the absence of any unchanged acetonylnitrophenol was assured and the clear red solution was acidified with hydrochloric acid, the dinitrodioxydiphenyl being precipitated in a white, flocculent form. The yield was approximately 75 per cent of the theoretical. Dinitrodioxydiphenyl may be precipitated from its neutral or slightly alkaline solutions by means of carbon dioxide, but the presence of more than a very slight amount of alkali prevents this precipitation in dilute solutions. Under these conditions acetonylnitro-

phenol, if present, will be precipitated and may consequently be removed. The product may be advantageously crystallized from its solution in acetone to which a little ligroin is afterward added. The crystals appear in small colorless needles, and melt, when pure, at 301° (corr.). This dinitrodioxydiphenyl is readily soluble in alcohol, ethyl acetate, hot acetone, or hot glacial acetic acid. It is only sparingly soluble in ether, chloroform, or hot water, and practically insoluble in benzol, ligroin, or carbon disulphide.

I. 0.1268 gram substance gave 0.2420 gram CO_2 and 0.0376 gram H_2O.

II. 0.2088 gram substance gave 19.8 cc. moist N at 22° and 740.3 mm. pressure.

	Calculated for $C_{12}H_8N_2O_6$.	Found. I.	Found. II.
C	52.16	52.05	...
H	2.92	3.31	...
N	10.17	...	10.41

A compound of this type but not of this constitution has been described by Kunze.[1] It is a dinitro derivative of paradiphenol obtained by nitration of the latter, whereas the substance we describe is derived from orthodiphenol. The properties of the two compounds are, as might be expected, somewhat similar. Another nitrodiphenol has been obtained by the action of potassium permanganate upon orthonitrophenol.[2] Its constitution, however, has not been determined. Presumably, the hydroxyl groups are not in the ortho position. A single experiment in which the action of potassium permanganate upon paranitrophenol was carried out as Goldstein directs for the orthonitrophenol did not give our dinitrodioxydiphenyl, which would have been formed if the oxidation and condensation had taken place at the ortho position to the hydroxyl group. The preparation of 3,3′-dinitro-6, 6′-dioxydiphenyl was indeed the primary object of this investigation. Its preparation has resulted from the synthesis of each benzol molecule in order, but the simultaneous synthesis of the two benzol rings, as anticipated, might have been possible if we had not been dealing with strongly negative substituents. In this case further condensation can be effected only by the use of strong condensing agents, which, if employed at the first stage, would have resulted in the simultaneous condensation just mentioned. That we might further check the results of our work, a few derivatives of this dinitrodioxydiphenyl have been prepared. Owing to the small amount of material at our disposal, the salts of the diphenol were not studied. They may be prepared, however, by the usual methods. They dissolve readily in water, imparting a deep red color to the solution, a characteristic of this class of phenols.

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[1] Ber. d. chem. Ges., **21**, 3331 (1888).

[2] Goldstein: J. Russ. Chem. Soc., **6**, 193 (1874).

3,3′-Diamino-6,6′-dioxydiphenyl, $(HO)(NH_2)C_6H_3.C_6H_3(NH_2)(OH)$.—The reduction of the dinitro derivative to the corresponding diamino form is easily accomplished by dissolving the former in warm, diluted alcohol and adding tin and concentrated hydrochloric acid. In the course of half an hour the reduction is complete and the clear solution, diluted with an equal volume of water, may be evaporated to small bulk over the steam bath to drive off the alcohol. After a further dilution of this residue with water, a current of hydrogen sulphide is passed through the hot liquid until all the tin is removed as sulphide. The clear filtrate gave, upon evaporation, long, colorless prisms of the hydrochlorate of this amino derivative. This hydrochlorate was transformed into the free body by bringing it into solution with water and just neutralizing with potassium carbonate solution, when the free diaminodioxydiphenyl is precipitated and may be filtered off at once. The yield is about 85 per cent of the theoretical. Diaminodioxydiphenyl is only sparingly soluble in hot alcohol and insoluble in almost all of the ordinary media. Its purification was therefore not attempted.

Oxidation of 3,3′-Diamino-6,6′-dioxydiphenyl to Diquinone, $C_6H_3O_2.C_6H_3O_2$.—Two and two-tenths grams (1 molecules) of the diamino derivative was dissolved in ten times its weight of diluted sulphuric acid (1 part acid to 3 parts water by weight). To this solution, 3.6 grams ($1^1/_4$ molecules) sodium dichromate in 16 cc. of water were added, and the mixture warmed very gently. The glistening, yellow crystals of the diquinone separated almost immediately, and were filtered off and dried. The yield was about 60 per cent of the theoretical. Diquinone crystallizes best from glacial acetic acid in small prisms of a light-lemon color. It crystallizes also in fine, long prisms from ethyl acetate. The pure substance melts at 192° (corr.). Diquinone is extremely soluble in acetone; fairly soluble in benzol, chloroform, or alcohol; but slightly soluble in ether; and insoluble in ligroin. It dissolves sparingly in hot water from which it crystallizes on cooling.

0.1298 gram substance gave 0.3196 gram CO_2, and 0.0344 gram H_2O.

	Calculated for $C_{12}H_6O_4$.	Found.
C	67.28	67.14
H	2.82	2.96

This product is identical with the diquinone described by Barth and Schreder,[1] who, however, found a slightly lower melting point, 186-187° (uncorr.).

Reduction of Diquinone to Dihydroquinone, $(HO)_2C_6H_3.C_6H_3(OH)_2$.—When 2 grams of the diquinone were suspended in water, a current of sulphur dioxide led through the vessel for a half hour or more to complete saturation, and the vessel then stoppered and set aside for a few hours, the reduction of the diquinone was accomplished. From the clear solution, the dihydroquinone may be extracted with ether. The dihydroquinone thus obtained can be crystallized from a small quantity of water containing sulphur dioxide, which will prevent any possible reoxidation to the quinone. Several recrystallizations are necessary before a product of sufficient purity can be obtained. The pure product appears in the form of colorless prisms melting at 237°-238° (uncorr.) with decomposition. It is readily soluble in alcohol, acetone or ethyl acetate; fairly soluble in ether or hot water; slightly soluble in chloroform or benzol; and insoluble in ligroin.

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[1] Monats. Chem., 5, 603 (1884).

This dihydroquinone is sweet to the taste; colored red in aqueous solution by ferric chloride; and in all other respects, identical with the dihydroquinone described by Barth and Schreder.[1] The identity of both the diquinone and dihydroquinone with those described by Barth and Schreder further serves to establish the constitution assigned to the condensation products just studied. The preparation of the dinitrodioxydiphenyl by the method described above affords also a simple means for the preparation of its monoalkyl ethers.

3,3′-Dinitro-6,6′-dioxydiphenyl Dimethyl Ether, $(CH_3O)(NO_2)C_6H_3.C_6H_3(NO_2)(OCH_3)$.—A small quantity of the dinitrodioxyphenyl was brought into solution in water in the form of a sodium salt with the aid of an excess of sodium hydroxide. To this strong alkaline solution was added a little dimethyl sulphate and the vessel well shaken, with warming. In a few minutes a white precipitate separates. This is removed by filtration and thoroughly digested with a warm solution of sodium carbonate in order to remove any unchanged diphenol. The crude product thus obtained is conveniently purified by crystallization from acetone and ligroin from which it separates in small needles melting at 264° (corr.). The dimethyl ether of dinitrodioxydiphenyl is readily soluble in warm acetone, chloroform, alcohol, or ethyl acetate, and fairly soluble in benzol. It is insoluble in ligroin or water.

I. 0.1382 gram substance gave 0.2788 gram CO_2 and 0.0516 gram H_2O.

II. 0.2428 gram substance gave 20.9 cc. moist N at 22.4° and 736.4 mm. pressure.

	Calculated for $C_{14}H_{12}O_6N_2$.	Found. I.	II.
C	55.24	55.03	...
H	3.97	4.18	...
N	9.23	...	9.38

3,3′-Dinitro-6,6′-dioxydiphenyl Diethyl Ether, $(C_2H_5O)(NO_2)C_6H_3.C_6H_3(NO_2)OC_2H_5$.—The diethyl ether of dinitrodioxydiphenyl may be prepared by converting the free diphenol into its sodium salt, dissolving the dried salt in ethyl alcohol to which ethyl iodide has been added, and boiling the solution for several hours under a reflux condenser over a water bath. The clear liquid thus obtained is evaporated to dryness and the mass extracted with ether, in which the diethyl ether is slowly taken up. Crystallization from acetone or from ethyl acetate gave needle clusters with a melting point of 271° (corr.). The diethyl ether is fairly soluble in warm acetone, alcohol, chloroform or ethyl acetate; only slightly soluble in ether or hot benzol; and insoluble in ligroin or water. It resembles very closely the dimethyl ether.

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[1] Monats. Chem., 5, 600 (1884).

I. 0.1202 gram substance gave 0.2542 gram CO_2 and 0.0536 gram H_2O.

II. 0.2216 gram substance gave 17.5 cc. moist N at 23.8° and 741.4 mm. pressure.

	Calculated for $C_{16}H_{16}O_6N_2$.	Found. I.	II.
C	57.80	57.68	...
H	4.85	4.99	...
N	8.45	...	8.60

3,3′-Dinitro-6,6′-dioxydiphenyl Monoethyl Ether, $(HO)(NO_2)C_6H_4.C_6H_3(NO_2)OC_2H_5$.—The preparation of this ether is accomplished through the condensation of the ethyl ether of acetonylnitrophenol with nitromalonic aldehyde. The condensation is carried out by dissolving one molecule of acetonylnitrophenol ethyl ether in alcohol and adding the solution to one molecule of sodium nitromalonic aldehyde in a small quantity of water containing a little sodium hydroxide. The addition of more than one molecule of alkali, the amount required for the condensation of the free acetonylnitrophenol and sodium nitromalonic aldehyde, is not necessary. The operation requires from 2 to 3 days for its completion. The final red solution was extracted with ether, in order to remove any unchanged ethyl ether of acetonylnitrophenol and then acidified with hydrochloric acid, when a flocculent white precipitate of the monoethyl ether appeared. The yield was about 75 per cent of the theoretical. The monoethyl ether is very soluble in warm acetone, alcohol or ethyl acetate;

fairly soluble in warm chloroform or benzol; and insoluble in ligroin or water. It crystallizes from acetone in colorless, fine, silky needles which mat closely together. The melting point is 224° (corr.).

I. 0.1552 gram substance gave 0.3136 gram CO_2 and 0.0569 gram H_2O.

II. 0.2848 gram substance gave 24.1 cc. moist N at 20.8° and 738.7 mm. pressure.

	Calculated for $C_{14}H_{12}O_6N_2$.	Found. I.	II.
C	55.24	55.11	...
H	3.97	4.10	...
N	9.23	.....	9.32

The condensation of the alkylated acetonylnitrophenol with nitromalonic aldehyde requires but little alkali as a condensing agent. The use of a larger amount somewhat facilitates the reaction and hence its employment in the above case. The presence, therefore, of the ethoxyl group in the phenyl ring is seen to have a much smaller retarding action upon the further condensation of the acetonyl group than has the hydroxyl group in the same substituent. The condensations which are possible in the use of the diketone, acetonylacetone, have proved of much interest in the study of dialdehydes, and will, it is hoped, still further enlarge the possibilities of these ring formations when the constitution of the compound now under study is established and its formation explained. For the kind services of Mr. A. C. Houghton in aiding and furthering this work, we wish to express our appreciation and gratitude.

Ann Arbor, Michigan,
Nov. 1, 1907.

[Contributions from the Chemical Laboratory of Harvard College.]

ROSOCYANINE.

By Latham Clarke and C. Loring Jackson.

The reaction of turmeric paper with boric acid was observed,[1] and used as a test for this substance, even before the first attempt[1] to study curcumine, the yellow coloring matter of turmeric, but in spite of this early discovery, very little attention has been paid to the nature of this interesting reaction. So far as we can find, only two men have tried to study it. The first paper on this subject was by Schlumberger,[2] in which he described the preparation and properties of the substance formed by the action of boric acid and a strong acid on curcumine in alcoholic solution, and called it rosocyanine from its crimson rose color in solution and its blue salts. He stated that it contains no boron, and that on boiling it with alcohol, a resinous substance, called by him pseudocurcumine, was produced, from which he could obtain neither curcumine nor rosocyanine. Curcumine, when boiled with boric acid and alcohol, formed a vermilion product containing boric acid which was given up on boiling with water, leaving pseudocurcumine. This vermilion substance gave a purple color with alkalies, and rosocyanine with acids. His paper contains no analyses. Considering the very impure curcumine used by him, his results are surprisingly accurate; the few mistakes will be pointed out in the description of the similar experiments tried by us.

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[1] Trommsdorff: Trommsdorff's J. v. Pharm., **16**, 96. Sementini: Bibliothéque Britannique, January, 1815.

Six years later, Ivanow-Gajewski[3] took up the study of rosocyanine in connection with his research on curcumine. The meagre abstracts of his papers, which alone are accessible to us, state that he analyzed rosocyanine, but failed to establish any satisfactory formula for it, which is not surprising, as at that time he was working with a very impure curcumine melting at 140° (instead of 178°[4] or 183°[5]). The next year he stated[6] that rosocyanine contains no boron, and that, fused with potassic hydrate, it yields paraoxybenzoic acid. This last observation, if correct, is of no value in determining the constitution of rosocyanine, because our experiments show that it contains the unaltered vanillin group of curcumine.

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[1] A. Vogel, Sr., and Pelletier: J. de. Pharm., **1**, 289.

[2] Bull. Soc. Chim. [2], **5**, 194 (1866).

[3] Ber. d. chem. Ges. **5**, 1103 (1872).

[4] Jackson and Menke: THIS JOURNAL, **4**, 77.

[5] Ciamician and Silber: Gazz. chim. ital., **27**, I, 561 (1897).

[6] Ber. d. chem. Ges., **6**, 196 (1873).

It is strange that this reaction has not attracted more attention, for it is certainly one of the most curious in organic chemistry, and is familiar to all chemists. How does the boric acid modify the molecule of curcumine? And why should boric acid alone[1] act in this way? We have made some progress toward answering these questions and have decided to publish our results now instead of waiting until we can give a more complete answer, because this cannot be done before the constitution of curcumine is determined, and owing to the unmanageable nature of its derivatives, like all others who have worked in this field we have found that the research advances with extreme slowness, so that it will be a long time before we can bring our work on rosocyanine to a conclusion.

The most obvious answer to the questions proposed above would be that the boric acid formed a compound with curcumine, and this supposition has been advanced by Ostwald in his "Scientific Foundations of Analytical Chemistry,"[2] but, as the only men who had worked with this substance, Schlumberger and Ivanow-Gajewsky, both had stated that it contains no boron, Ostwald's hypothesis, when proposed, was contrary to the observed facts, and as our experiments amply confirm these statements of our predecessors, it must be rejected.

The rosocyanine used by us was prepared from pure curcumine by heating it with boric acid and sulphuric acid in alcoholic solution. It was freed from mineral impurities by washing with water, from unaltered curcumine with ether, in which rosocyanine is insoluble. Although Schlumberger says he prepared it in fine needles, we have not yet succeeded in obtaining it in crystals, but it appears as a purple powder looking much like rosaniline except that the green metallic reflex has a yellower tinge. It decomposes without melting between 200° and 230°, dissolves in alcohol, forming a crimson rose solution, free from even a trace of magenta, and forms salts of a pure and beautiful blue color.

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[1] The coloration produced on turmeric paper by a solution of zirconic oxide in hydrochloric acid seems to be caused by something else than rosocyanine to judge from Brush's account of it [J. prakt. Chem., **62**, 7 (1854)]; and so far as we know it has not been proved that rosocyanine is formed by the action on turmeric paper of compounds of titaniun, molybdenum, niobium, or tantalum. We hope to study these reactions later.

[2] M'Gowan's translation, p. 209 (1900).

The absence of boron was proved by a qualitative test, which was shown by special experiments to be delicate enough to detect the boron if it was present as an essential constituent, and also even more definitely by the combustions of rosocyanine, which gave the same percentages of carbon and hydrogen as those in curcumine. A molecular weight determination showed that it is an isomer, not a polymer, of curcumine, and its formula[1] is, therefore, $C_{14}H_{14}O_4$.

Only one salt of rosocyanine, $C_{14}H_{13}RO_4$, could be obtained with an alkali, whereas curcumine gives two, $C_{14}H_{13}RO_4$ and $C_{14}H_{12}R_2O_4$. It is evident, therefore, that one of the hydroxyl groups of the curcumine takes part in the formation of rosocyanine, and to determine which of the two it was, the monomethylcurcumine was prepared from the potassium salt made from potassic carbonate, so that in this case the more acid of the two hydroxyls was converted into a methoxyl. This monomethyl ether gave the rosocyanine reaction, as shown by the characteristic crimson color of the alcoholic solution of the product, but, as was expected, the monomethylrosocyanine formed no salts. As, however, the position of this more acid hydroxyl in curcumine had not been as yet determined, we oxidized the monomethylcurcumine, and obtained veratric acid, $C_6H_3(OCH_3)_2COOH$; this more acid hydroxyl, therefore, is attached to the benzene ring, in other words, is the vanillin hydroxyl, which is in harmony with the fact that salts of vanillin can be formed by the decomposition of carbonates. It follows from these experiments that the hydroxyl which takes part in the rosocyanine reaction is the less acid one on the side chain, the benzene nucleus probably taking no part in the reaction. This view was supported by the observations that the dimethyl ether of curcumine, $C_{14}H_{12}(CH_3)_2O_4$, gave no rosocyanine, and that protocurcumine, $C_6H_3(OH)_2C_7H_7O_2$, gave the rosocyanine reaction.

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[1] We have proved (Ber. d. chem. Ges., **38**, 2712; **39**, 2269) that the formula of curcumine is $C_{14}H_{14}O_4$ and not the $C_{21}H_{20}O_6$ ascribed to it by Ciamician and Silber (Gazz. chim. ital., **27**, I, 561).

The facts that rosocyanine forms one salt and curcumine two indicate that in rosocyanine the second curcumine hydroxyl has been modified in some way. This modification might consist in the conversion of the hydroxyl into (*a*) a less acid (more alcoholic) hydroxyl, (*b*) a keto or aldehyde group, or (*c*) an oxide. (*a*) Rosocyanine forms only a monacetic ester, $C_{14}H_{13}(C_2H_3O)O_4$, which indicates that it contains only one (the vanillin) hydroxyl, but this indication cannot be accepted definitely until the acet compounds of curcumine have been submitted to a revision,[1] because Menke and one of us[2] found that the usual product of the action of acetic anhydride and sodic acetate on curcumine was a viscous monacetcurcumine, only one preparation out of many, giving a crystallized diacetcurcumine melting at 154°, and Ciamician and Silber,[3] by the action of acetic anhydride, obtained a monacetcurcumine which they succeeded in crystallizing, when it melted at 170°-171°. As there is no doubt that curcumine contains two hydroxyls, these experiments seem to show that one of these may escape the action of the acetic anhydride, and it is possible, although improbable, that the same may be true of rosocyanine. (*b*) As hydroxylamine hydrochloride has no action on rosocyanine, no ketone or aldehyde can have been formed. (*c*) It follows, therefore, that the oxygen of the less acid (side chain) hydroxyl of the curcumine must have been converted into the oxide form, provided further experiments show that our reasoning in the case of the hydroxyl (*a*) is correct.

The dihydride of curcumine, $C_{14}H_{16}O_4$, gave no rosocyanine reaction. In this dihydride, the hydrogen is probably added to one of the double bonds, although we cannot yet give an experimental proof of this; in that case the double bond also takes part in the rosocyanine reaction.

If rosocyanine is allowed to stand with an aqueous solution of potassic hydrate in the cold, in a short time it is converted back into curcumine. Under similar conditions the monomethylrosocyanine gives monomethylcurcumine.

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[1] A temporary lack of material compels us to postpone this revision to a later paper.

[2] THIS JOURNAL, **6**, 77 (1884-5).

[3] Gazz. chim. ital., **27**, I, 561 (1897).

It would not be hard to write a formula for rosocyanine based on the observations described above, but we think it wiser to postpone this until our further researches on curcumine have provided a safe experimental basis for such a formula, especially as it must also account for rubrocurcumine, which will be described presently.

In the hope of answering the question why only boric acid should give the rosocyanine reaction we have tried to isolate the intermediate products between curcumine and rosocyanine, and for this purpose have taken up the study of the red substance formed, according to Schlumberger,[1] by the action of boric acid and alcohol on curcumine. We soon found that there are two red products of this reaction, which Schlumberger could hardly have distinguished, as he made no analyses. The more stable is obtained by precipitation with water; it has a full vermilion color, is free from boron, and contains percentages of carbon and hydrogen corresponding to the formula $C_{14}H_{14}O_4$. That it is not a mixture of curcumine and rosocyanine (which also have this formula) is proved by its color, and especially by the facts that it is much more soluble in alcohol than either of these bodies, and gives an acet compound, $C_{14}H_{13}(C_2H_3O)O_4$, of an orange red color which crystallizes well and has a constant melting point of 245°. Acetcurcumine[2] melts at 170°-171°, diacetcurcumine[3] at 154°, and acetrosocyanine does not melt.

Rubrocurcumine, as we propose to name this substance, shows but a slight stability, passing back to curcumine on standing at ordinary temperatures for two weeks, while, on boiling with water, the same change takes place in a few minutes. Schlumberger, under these conditions, obtained his supposititious pseudocurcumine, which was probably curcumine mixed with a large amount of resinous impurity from the turmeric. Between 200° and 240°, the rubrocurcumine is converted into rosocyanine, and the same change is produced very easily by warming it with dilute sulphuric acid. With an aqueous alkali, the rubrocurcumine gives a royal purple solution, but this quickly changes color, a salt of curcumine being apparently formed.

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[1] Bull. Soc. Chim. [2], **5**, 194 (1866).

[2] Ciamician and Silber: Gazz. chim. ital., **27**, I, 561 (1897).

[3] This Journal, **6**, 78 (1884-5).

The other product of this reaction is obtained when the alcoholic solution of boric acid and curcumine, after the reaction has taken place, is precipitated with ether instead of water. It has a somewhat deeper red color than rubrocurcumine, but could hardly be distinguished from it by the eye alone. It seems to be an addition compound of boric acid and curcumine, but we have not yet brought it into a state fit for analysis. That it is not a mixture of boric acid with rubrocurcumine, rosocyanine, or curcumine is shown by the fact that on standing it is converted, in a short time, into a waxy mass, a property shown by none of those three compounds. Water decomposes it at once into rubrocurcumine and boric acid.

There is no doubt, we think, that this addition compound is formed at first in the preparation of rosocyanine from curcumine. Whether it is converted into rosocyanine directly, or into rubrocurcumine, which the sulphuric acid then changes to rosocyanine, cannot be decided with our present data. The intermediate formation of rubrocurcumine certainly seems probable, but we have no experimental proof that this action can be brought about by the reagents present—hot alcohol, sulphuric acid, and the small amount of water used to dilute it. Our next experiments in this line will deal with this subject, the establishment of the composition of the addition product and the determination of the constitution of curcumine, rosocyanine, and rubrocurcumine.

Some experiments on the preparation of rubrocurcumine and rosocyanine showed that the presence of water was unfavorable to both these reactions, and that rosocyanine can be formed when pure acetone or glacial acetic acid is substituted for the alcohol, so that this seems to act only as a solvent. Glacial acetic acid can also take the place of the sulphuric (or hydrochloric) acid, and it can be replaced also by mannite or glycerine in the preparation of rosocyanine, although in these latter cases the effect of the strong acid is probably obtained from the boric acid, intensified by the polyatomic alcohol.

F. Emich, in a paper[1] contributed to the Lieben-Festschrift, makes the following statement: "Färbt man z. B. Schafwolle, Seide, oder Schiesswolle mit Curcumatinctur, so entsteht nach der Behandlung mit angesäuerter Boraxlösung wohl eine Roth- oder Braunfärbung beim Eintrocken, *aber keine Bläuung mit Soda* (höchstens eine dunklere Braunfärbung). Die Bläuung tritt nur auf, wenn man den Farbstoff auf Papier, Baumwolle, oder Leinenfaser niederschlägt. Es scheint sich also um eine Reaction der Cellulose zu handeln." This inference of Emich's, that the blue color is due to a reaction of cellulose, is disproved by our results, as we have repeatedly made rosocyanine and its blue salts under conditions where no cellulose was present, but in consideration of this definite statement of his, that the blue coloration is not obtained on wool, we have felt obliged to try the following experiment: A piece of white woolen cloth was dyed with an alcoholic solution of curcumine, and after drying, treated with a mixture of dilute sulphuric acid and boric acid. On drying at 100°, the wool took on a crimson color, which turned to a dark, vivid blue when treated with dilute sodic hydrate or ammonic hydrate. As we, therefore, found no difficulty whatever in obtaining the rosocyanine reaction on wool, we have not thought it worth while to repeat the experiment with silk or gun cotton.

EXPERIMENTAL.

Preparation of Rosocyanine.—After several experiments the following method of preparation proved the most convenient.

Four grams of sulphuric acid (specific gravity 1.84) were poured into 80 cc. of alcohol, and to the mixture, 4 grams of crystallized boric acid and 4 grams of curcumine (purified by crystallization from alcohol and melting at 178°) were added. The whole was then heated on the water bath in a flask with a return condenser, when, after a few seconds, the solution took on a deep crimson color, and all the curcumine and boric acid went into solution. After the heating had been continued for three or four hours, yellowish green metallic patches of nearly pure rosocyanine appeared adhering to the sides of the flask. The hot solution was then poured into 400 cc. of water, and the precipitate thus formed filtered out, washed with water till free from acid, and dried. This product was a fine greenish powder consisting essentially of a mixture of rosocyanine and unchanged curcumine. We tried at first to remove the curcumine by dissolving the product in alcohol and precipitating with ether, in which rosocyanine is insoluble, but the precipitate formed was so finely divided as to be unmanageable. Accordingly the crude product was extracted for six hours with ether, and then in order to remove any curcumine which was protected from solution by a coating of rosocyanine, the residue was dissolved in alcohol, and precipitated by pouring it into three to four times its volume of a two per cent solution of sodic chloride. If no salt was used in the water, the rosocyanine appeared in such a finely divided form that it was impossible to wash it. The new precipitate was washed thoroughly with water, dried, and extracted again with ether until it ceased to give a colored solution.

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[1] Ann. Chem. (Liebig), **351**, 429 (1907).

The rosocyanine obtained in this way was pure, as far as we could find. The yield was about 80 per cent of the weight of the curcumine. By using absolute instead of common alcohol, in some cases the yield was raised to 95 per cent, but we did not find this gain in yield sufficient to make up for the trouble of preparing absolute alcohol, and therefore used common alcohol in most of our preparations. The addition of water, on the other hand, diminished the yield, as with a mixture of equal parts of alcohol and water 60 per cent was the best we could obtain. Other modifications of the process also led to poorer results, although a certain amount of rosocyanine can be obtained under a great variety of conditions. Rosocyanine can be prepared to advantage from the viscous residues left by the evaporation of the alcoholic mother liquors from the purification of crude curcumine. Upon treating this impure mass with alcohol, sulphuric acid, and boric acid, as described above, rosocyanine is formed, which is easily freed from the resinous impurity by washing with ether. Although rosocyanine can be converted into curcumine by standing with aqueous sodic hydrate, it is not practicable in this way to increase the yield of curcumine from turmeric, because this conversion is far from quantitalive.

Composition of Rosocyanine.

Both Schlumberger[1] and Ivanow-Gajewsky[2] state that rosocyanine contains no boron, but, as we have seen no account of the experimental methods used by them, we thought it necessary to test our rosocyanine for boron as follows: A quantity of it was fused with a mixture of sodic carbonate and potassic nitrate until all the organic matter had been decomposed, the residue was then dissolved in water, acidified with hydrochloric acid, and tested for boric acid with turmeric paper, when the result was entirely negative.

To show that boric acid, if present, would have been detected by this method, 1 gram of rosocyanine was mixed with 0.05 gram of boric acid, and upon submitting it to the same treatment a strong test for boric acid was obtained. Also 0.2642 gram of boric acid mixed with about 0.6 gram of rosocyanine were fused with a mixture of 10 parts of sodic carbonate and 5 of potassic nitrate. The residue was dissolved in water, acidified with hydrochloric acid, and the excess of acid destroyed with a mixture of 4 parts of potassic iodide to one of potassic iodate, the liberated iodine removed by treatment with sodic thiosulphate, and the free boric acid titrated by the mannite method of L. C. Jones;[3] the amount found was 0.2508 gram instead of 0.2642 gram. This agreement between the weight of acid used and that recovered is as close as could be expected, since, owing to the danger of decomposing the boric acid, no very complete drying of the original amount was attempted. We have not studied the subject further, as these two experiments are sufficient to show that the method is accurate enough for our purpose, and the absence of boron was rendered absolutely certain by the following combustions of rosocyanine, which show that it has the same composition as curcumine. The substance burnt with great difficulty, so that in each analysis a portion of the carbon was weighed as such.

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[1] Bull. Soc. Chim. [2], **5**, 194 (1866).

[2] Ber. d. chem. Ges., **6**, 196 (1873).

[3] Am. J. Sci. [4], **7**, 147 (1899).

I. 0.1278 gram substance gave 0.2988 gram CO_2, 0.0058 gram C, 0.0659 gram H_2O.

II. 2.2301 gram substance gave 0.5170 gram CO_2, 0.0148 gram C, 0.1126 gram H_2O.

III. 0.1347 gram substance gave 0.3001 gram CO_2, 0.0094 gram C, 0.0660 gram H_2O.

	Calculated for $C_{14}H_{14}O_4$.	Found.		
		I.	II.	III.
C	68.29	67.82	67.71	67.74
H	5.69	5.69	5.43	5.44

It is a noteworthy fact that the percentages of hydrogen are low in all these combustions. The same observation was made in the analyses of curcumine carried out for the first paper[1] on this subject by Menke and one of us, but a formula with less hydrogen would give results which do not agree with those found by experiment.

The molecular weight was determined in boiling acetone.

0.1041 gram substance dissolved in 35 grams acetone gave $\Delta = 0.02°$, $K = 1670$.

	Calculated for $C_{14}H_{14}O_4$.	Found.
Mol. Wt.	246.0	248.0

Properties of Rosocyanine.

Although Schlumberger states that he got fine needles, we have not succeeded in crystallizing the substance, but obtained it as a purple powder with a metallic, yellowish green reflex, which shows a close resemblance to powdered rosaniline except that the green color is yellower. A thin film of it deposited from an alcoholic solution shows a beautiful crimson rose color by transmitted light, which has no shade of magenta in it, while by reflected light it is yellowish green with a metallic lustre. It does not melt, but at about 230° changes to a greenish black substance, insoluble in alcohol, but dissolving in aqueous sodic hydrate with a bluish black color, which changes on standing to yellowish brown. This transformation of the rosocyanine begins at 200°, but goes on slowly as long as the temperature is much below 230°. On the other hand the substance should not be heated far above 230°, as in the neighborhood of 260° it decomposes into a black carbonaceous residue and a volatile red oil, which condenses in the upper part of the capillary tube, while at the same time a penetrating odor is observed. If the rosocyanine is not perfectly dry, between 230° and 260° a colorless liquid is given off, which differs from the oil both in color and smell. The study of these products will be taken up by us later. Rosocyanine is moderately soluble in ethyl alcohol, somewhat less soluble in methyl alcohol, acetone, or glacial acetic acid. All these solutions are characterized by a beautiful crimson rose color without a trace of magenta. It is not decomposed by alcohol, contrary to the statement of Schlumberger. It is almost insoluble in acetic ester, and essentially insoluble in ether, benzene, toluene, chloroform, or carbon tetrachloride. Strong sulphuric acid forms a red solution with it, from which the rosocyanine is precipitated apparently unchanged on dilution. Strong nitric acid also forms a red solution with it, but strong hydrochloric acid produces no apparent effect.

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[1] THIS JOURNAL, **4**, 77 (1882).

Its behavior with alkalies is very characteristic. If aqueous sodic hydrate is added to solid rosocyanine, a magnificent bluish purple solution is formed, having the color of Hofmann's violet, but if the sodic hydrate is added to an alcoholic solution, the liquid takes on a blue color like that of the solution of Prussian blue in oxalic acid. Ammonic hydrate gives a similar Prussian blue solution even in the absence of alcohol.

As it was observed that the solution of rosocyanine in an excess of aqueous potassic or sodic hydrate turned green rapidly if the amount of alkali was large, slowly if it was small, the following experiment was tried to study this decomposition. Four grams of potassic hydrate were dissolved in a mixture of 10 cc. of alcohol with 30 cc. of water, and 0.2 gram of pure rosocyanine added. With so much alcohol present the rosocyanine dissolved very quickly, forming the characteristic fine blue solution of the salt, but in about three minutes the color had turned to green, in another three minutes it was brown, and in five minutes more it had become red. It was allowed to stand five more minutes (16 in all), and then acidified with dilute hydrochloric acid, the precipitate thus formed was washed with water, dried, and after two recrystallizations from alcohol formed yellow crystals, which, as they melted at 178° and formed a red potassium salt, must be curcumine. This experiment was repeated several times with the same result. There can be no doubt therefore that rosocyanine is converted into curcumine by standing in the cold with potassic hydrate. The hydrochloride of hydroxylamine has no action on rosocyanine.

Salts of Rosocyanine.

Ammonium Salt, $NH_4C_{14}H_{13}O_4$.—This was prepared by passing dry ammonia gas into an alcoholic solution of rosocyanine. The bluish green solution thus obtained deposited a blue precipitate, which was dried between filter papers for analysis.

0.3495 gram substance gave 15 cc. N at 20° and 760 mm.

	Calculated for $NH_4C_{14}H_{13}O_4$.	Found.
N	5.32	4.91

To judge from the blue color, this same salt was formed when a layer of rosocyanine, spread on a filter paper, was exposed to the vapor from strong ammonic hydrate by letting the two stand in a desiccator, but the action did not seem to be complete, even after it had been continued for a long time, so that this method cannot be recommended for making the salt.

Potassium Salt, $KC_{14}H_{13}O_4$.—To a saturated solution of rosocyanine in 25 cc. of absolute alcohol was added a solution of 0.2 gram of potassic hydrate in 10 cc. of alcohol. After the mixture had stood a moment, 5 or 6 drops of ether were added, when the salt separated in purple flocks, which were filtered out, washed first with absolute alcohol and then with ether, and dried *in vacuo* for analysis. The work must be carried on rapidly to avoid the decomposition of the rosocyanine by the excess of alcoholic potassic hydrate.

I. 0.1821 gram of salt gave 0.0562 gram K_2SO_4.

II. 0.0794 gram of salt gave 0.0246 gram K_2SO_4.

	Calculated for $KC_{14}H_{13}O_4$.	Found. I.	Found. II.
K	13.76	13.85	13.91

The potassium salt forms purple flocks, which are stable when dry, and dissolve easily in water with the characteristic blue color of the rosocyanine salts.

Barium Salt of Rosocyanine, $Ba(C_{14}H_{13}O_4)_2$.—An aqueous solution of baric hydrate was added, drop by drop, to an alcoholic solution of rosocyanine, and the beautiful blue flocculent precipitate thus obtained was filtered out, washed with alcohol, and dried *in vacuo* for analysis.

0.1204 gram of salt gave 0.0454 gram $BaSO_4$.

	Calculated for $Ba(C_{14}H_{13}O_4)_2$.	Found.
Ba	21.85	22.17

The dry salt has a purple blue color with a bronze reflex, and gives a violet mark on paper; when moistened with alcohol, it has a fine blue color. It is essentially insoluble in alcohol, and only very slightly soluble in water.

An aqueous solution of the potassium salt of rosocyanine gave characteristic precipitates with the following reagents: With calcic chloride, baric chloride, or magnesic sulphate, dark blue, the two latter precipitates being much darker than the first; with zincic sulphate, blue black; with cadmic sulphate, dark blue; with cobaltous nitrate, blue black; with nickelous nitrate, dark purple; with ferric chloride, aluminic sulphate, or chromic sulphate, dark red; with cupric sulphate or mercurous nitrate, dark red; with mercuric chloride, purple; with plumbic acetate, dark blue; with argentic nitrate, dark purple.

Acetrosocyanine, $C_{14}H_{13}(C_2H_3O)O_4$.—Two grams of rosocyanine with 30 grams of acetic anhydride were heated on the water bath to 60°, for 8 hours, in a flask with a return condenser. The liquid assumed a brownish red color as soon as the rosocyanine was added, which did not change during the eight hours' heating. At the end of that time the acetic anhydride solution was poured off from the undissolved solid and evaporated *in vacuo*, leaving a brownish red powder mixed with a little oil, which was removed by extraction with cold benzene. The powder was then dissolved in alcohol, when, as the solution evaporated, the acetrosocyanine was deposited as an amorphous brownish red powder, from which cold benzene extracted nothing. The solid which was not dissolved in the acetic anhydride also proved to be acetrosocyanine. The substance was dried *in vacuo* for analysis.

0.1241 gram substance gave 0.3031 gram CO_2 and 0.0624 gram H_2O.

	Calculated for $C_{14}H_{13}(C_2H_3O)O_4$.	Found.
C	66.67	66.59
H	5.55	5.58

Properties.—We have not succeeded in obtaining crystals of the acetrosocyanine, which appears as a brownish red powder. It has no melting point, but at 250° the color changes from reddish brown to greenish, and that a new substance has been formed is shown by the facts that it is insoluble in alcohol and unaffected by an alkali. Acetrosocyanine is very soluble in chloroform; moderately soluble in ethyl alcohol; somewhat soluble in acetone; all these solutions have a reddish brown color; essentially insoluble in ether, benzene, or ligroin. Strong sulphuric acid dissolves it partially, forming a bright red solution; strong nitric acid forms a yellow solution with it, but the action is very slow; strong hydrochloric acid does not dissolve it, but slowly imparts a darker color to the solid. An alcoholic solution of potassic hydrate decomposes it quickly, giving a greenish solution, which soon changes to yellow; a moderately strong aqueous solution of sodic hydrate produces the same effect slowly, whereas a dilute solution acts on it only after long standing.

Action of Curcumine with Boric Acid and Alcohol.

Probable Addition Compound.—When a mixture of ten parts of curcumine with one part of boric acid was allowed to stand in the cold with alcohol for eight hours, a red solution was formed, which, after being filtered off from undissolved curcumine, was poured into ether; in this way a fine red powder was obtained which was filtered out and washed with ether. This product contains a considerable amount of boric acid, which it gives up when treated with water, being converted into the rubrocurcumine described in the next section. Three analyses were made by treating a weighed quantity with water, filtering out the organic matter, and titrating the boric acid by the mannite method,[1] but they showed that the substance had not yet been brought into a state fit for analysis, as they gave 14.7, 28, and 26 per cent of HBO_2, respectively. Further experiments will be necessary to determine whether the substances contained an impurity of boric acid, and whether the agreement of these results with those for addition products with one and with two molecules of boric acid is more than accidental. Meanwhile, it is plain that this product is not a mixture of boric acid with curcumine, rubrocurcumine, or rosocyanine, because it is converted into a waxy substance on exposure to the air—a property not shown by any of the three compounds mentioned.

Rubrocurcumine, $C_{14}H_{14}O_4$.—Two grams of curcumine, 2 grams of boric acid, and 20 grams of alcohol (95 per cent) were mixed together and allowed to stand overnight in a corked flask at ordinary temperatures. The clear red solution thus obtained was poured into 100 cc. of water, which decomposed the boric acid addition product and precipitated the rubrocurcumine in red flocks; these were quickly filtered out, washed with water until free from boric acid, and dried in a desiccator for analysis. In our earlier preparations a more elaborate method was used, consisting in evaporating the red alcoholic solution in a desiccator at ordinary temperatures until the rubrocurcumine began to form a crust on the edge of the dish, when the solution was poured into 20 cc. of ether and the precipitated rubrocurcumine washed with water as before. The object of this treatment was to remove any unaltered curcumine, but was proved to be unnecessary, because the amount of boric acid used was enough to convert all the curcumine into rubrocurcumine.

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[1] L. C. Jones: Am. J. Sci. [4], 7, 147 (1899).

0.0737 gram substance gave 0.1662 gram CO_2, 0.0049 gram C, and 0.0392 gram H_2O.

	Calculated for $C_{14}H_{14}O_4$.	Found.
C	68.29	68.15
H	5.69	5.90

Properties of Rubrocurcumine.—It was not obtained in crystals, but forms a vermilion powder of a less dark red color than the addition product. It appears to be unstable, as a sample, on standing at ordinary temperatures for two weeks, passed back into curcumine to judge from its behavior with dilute sulphuric acid or alkalies. The same change to curcumine takes place in a few minutes when rubrocurcumine is boiled with water. It does not melt, but, when heated to 200°, gradually takes on the purple color with a metallic green reflex of rosocyanine; at 240° the change takes place more rapidly and completely. That the product was rosocyanine was shown by the crimson rose color of its alcoholic solution and the intense blue color which appeared when it was treated with an alkali. If the temperature is carried to 250° or higher, a product insoluble in alcohol is formed, which dissolves in alkalies with a greenish color, and is probably identical with the substance obtained by heating rosocyanine. Heating rubrocurcumine with dilute sulphuric acid converts it easily into rosocyanine; but it is hardly necessary to state that these reactions can be obtained only with fresh, unaltered preparations. It is very soluble in alcohol, giving a red solution distinct in color from the crimson rose solution of rosocyanine; soluble in methyl alcohol, ether, or acetone; somewhat soluble in chloroform; almost insoluble in benzene or toluene. Strong sulphuric acid dissolves it with a bright red color; strong nitric acid forms with it a yellow solution; strong hydrochloric acid dissolves it only slightly, giving a violet solution changing very quickly to red. An aqueous solution of an alkali dissolves the rubrocurcumine with a royal purple color, that is, the solution is of a redder purple than that of the salt of rosocyanine. This solution quickly changes its color to brown, the rubrocurcumine apparently being converted into curcumine.

Acetrubrocurcumine, $C_{14}H_{13}(C_2H_3O)O_4$.—One gram of rubrocurcumine was allowed to stand at ordinary temperatures with 10 grams of acetic anhydride for 8 hours. The rubrocurcumine went into solution in less than half an hour, forming a yellowish red liquid. The acetic anhydride was evaporated off in a desiccator over sodic hydrate, and the yellow powder left recrystallized from alcohol till it showed the constant melting point, 245°, when it was dried *in vacuo* for analysis.

0.1479 gram substance gave 0.3315 gram CO_2, 0.0084 gram C, and 0.0756 gram H_2O.

	Calculated for $C_{14}H_{13}(C_2H_3O)O_4$.	Found.
C	66.67	66.81
H	5.55	5.68

Properties of Acetrubrocurcumine.—It forms orange yellow prismatic needles, which melt at 245°. The fact that this acet compound melts, whereas rubrocurcumine itself is infusible, may be explained on the supposition that in the latter body the hydroxyl is converted into the oxide oxygen of the infusible rosocyanine at a temperature below where its melting point would lie, whereas the acetoxyl of the former compound prevents its transformation into rosocyanine. Very soluble in acetone, or chloroform; somewhat soluble in methyl alcohol, ether, or glacial acetic acid; not very soluble in cold alcohol, more so in hot; slightly soluble in benzene; insoluble in ligroin. Strong sulphuric acid dissolves it with a bright red color; strong nitric acid gives a yellow solution with it; strong hydrochloric acid has no apparent effect. An aqueous solution of sodic hydrate has no effect on it in the cold, but, if heated with it, saponifies it, and then apparently converts it it into curcumine.

Experiments on the Preparation of Rubrocurcumine.

Under this head we have studied only the effect of water.

(1) One-tenth of a gram of curcumine was dissolved in absolute alcohol and 0.2 gram of boric acid added. The red color of rubrocurcumine appeared very soon, even in the cold, and a considerable amount of it was obtained after the mixture had stood for several hours in the cold or been heated for a few minutes.

(2) One-tenth of a gram of curcumine and 0.2 gram of boric acid were mixed with 10 cc. of a mixture of equal parts of alcohol and water. No rubrocurcumine was formed in the cold, even after standing for several weeks, but upon heating some of the mixture in a sealed tube to 160° for five hours fully 25 per cent of the curcumine was found to be converted into rubrocurcumine.

(3) The same weights of curcumine and boric acid were mixed with 10 cc. of water, but even after heating the mixture in a sealed tube to 160° for five hours only a very small amount of rubrocurcumine was formed.

These three experiments show that the presence of water interferes seriously with the formation of rubrocurcumine, but that it is possible to obtain it even without the help of alcohol.

Experiments on the Preparation of Rosocyanine.

The influence of water in preventing the formation of rosocyanine was shown in our preparations of it from curcumine, boric acid, sulphuric acid, and alcohol, where a yield of 95 per cent was obtained with absolute alcohol, 80 per cent with common (95 per cent) alcohol, and only 60 per cent with a mixture of equal parts of alcohol and water.

The alcohol used in the preparation of rosocyanine seems to take no part in the reaction, but to act only as a solvent, because a mixture of curcumine, boric acid, dilute sulphuric acid, and pure acetone gave rosocyanine, and it was also obtained from curcumine, boric acid, and glacial acetic acid, when the last substance not only acted as a solvent but also replaced the dilute sulphuric acid.

This experiment with acetic acid was tried before the discovery of rubrocurcumine had shown us that boric acid acts on curcumine in presence of alcohol alone, and formed part of a series on the influence upon the reaction of those substances which increase the acid nature of boric acid, and which we thought then might be necessary to cause the boric acid to unite with the curcumine. In addition to acetic acid, glycerine and mannite[1] act in this way, the last imparting to boric acid a taste as sour as that of citric acid and the power of decomposing carbonates. One gram of curcumine, one of boric acid, 0.5 gram of mannite, and 10 cc. of 50 per cent alcohol were warmed together for 5 minutes, when the solution had turned red, although not quite the pure crimson rose of rosocyanine, but on the addition of an alkali the intense blue, characteristic of the rosocyanine salts in alcoholic solution, was developed. For greater certainty it was compared with the color obtained by adding alkali to a solution of rosocyanine in 50 per cent alcohol, and found identical with it. Experiments such as this gave rosocyanine in three cases, but in a fourth only rubrocurcumine. Ten cc. of a 30 per cent solution of glycerine in water were mixed with 0.1 gram of curcumine, 0.2 gram of boric acid, and a few drops of alcohol. After standing in the cold for a few minutes the crimson color of rosocyanine appeared, and its presence was confirmed by the blue color produced with an alkali. The same result was obtained in a parallel experiment, in which the alcohol was omitted. These experiments show that mannite or glycerine can take the place of sulphuric or hydrochloric acid in the formation of rosocyanine. It seems probable, however, that the place of the strong mineral acid is taken by the boric acid, intensified by the mannite or glycerine, rather than by the polyatomic alcohols themselves.

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[1] L. C. Jones: Am. J. Sci. [4], **7**, 147; D. Klein: Bull. Soc. Chim. [2], **29**, 198 (1878); Lambert: Compt. rend., **108**, 1016 (1889).

Monomethylcurcumine, $C_6H_3(OCH_3)_2C_7H_7O_2$.—This substance was made from the monopotassium salt of curcumine discovered by Menke and one of us,[1] which we prepared as follows: Five grams of potassic carbonate and 5 grams of curcumine were boiled with 100 cc. of 99 per cent alcohol for half an hour, after which the deep red solution was filtered and 300 cc. of ether added to it, a few cc. at a time, with constant shaking. The monopotassium salt, which separated in fine red needles, was filtered out, washed with ether, and dried.

Three grams of this monopotassium salt were dissolved in 10 cc. of absolute methyl alcohol, 10 grams of methyl iodide added, and the mixture shaken on a shaking machine for 2 days. It was then allowed to stand in the cold for 2 days to give time for the crystallization of the potassic iodide, and, after this had been filtered out, the solution was evaporated *in vacuo*. The residue was a red tar, which, after standing for 2 days, hardened to a stiff mass; this was scraped out of the dish with a platinum spatula, thoroughly pulverized in a mortar, and washed with water until it gave no test for an iodide. Upon drying, it appeared as a brownish red powder which showed no sharp melting point. Accordingly, to purify it further, one gram was treated with 10 cc. of pure ether, the yellow solution thus formed evaporated *in vacuo*, and the extract, an orange colored oil, dissolved in 2 cc. of ordinary alcohol. The solution was filtered to remove some white needles, which appeared in such minute amount that we could not determine their nature, and then to the filtrate was added, drop by drop, with constant stirring, 20 cc. of a 20 per cent solution of sodic chloride in water. Under these conditions the monomethyl ether of curcumine crystallized out in very small, orange yellow needles, melting sharply at 145°, which were washed and dried *in vacuo*.

0.1355 gram substance gave 0.3441 gram CO_2 and 0.0751 gram H_2O.

	Calculated for $C_{14}H_{13}CH_3O_4$.	Found.
C	69.23	69.25
H	6.15	6.16

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[1] This Journal, 4, 77 (1882).

Properties of Monomethylcurcumine.—It crystallizes in small, orange yellow needles, which melt at 145°. It is soluble in ethyl or methyl alcohol, chloroform, acetone, benzene, acetic ester, or glacial acetic acid; somewhat soluble in ether; essentially insoluble in ligroin or carbon tetrachloride. It dissolves in aqueous sodic hydrate, owing to the formation of a soluble salt, but it is not acted on by sodic carbonate.

Oxidation of the Monomethylcurcumine.—As in this substance the methyl group had replaced the more acid atom of hydrogen, it was of interest to determine whether this was contained in a hydroxyl attached to the benzene ring or to the side chain. For this purpose the substance was oxidized as follows: One gram of the monomethyl ether of curcumine was dissolved in aqueous potassic hydrate, and a 5 per cent solution of potassic permanganate added in small quantities at a time. Decolorization took place at first quickly, later more slowly, and after a very slight excess had been added, the mixture was allowed to stand overnight. The permanganate was then destroyed by the addition of one or two drops of alcohol, the hydrate of manganese filtered out, thoroughly washed, and the filtrate, after acidification with dilute hydrochloric acid, extracted with ether. The ether extract, when evaporated to dryness, yielded a white powder which, after two recrystallizations from alcohol, showed the constant melting point, 178°. It is, therefore, veratric acid, the melting point of which is given by Graebe[1] and Borgmann and Koerner[2] as 179°.5, while Goldschmiedt[3] states that it softens at 179° and melts at 181°. Our somewhat lower result may easily be due to a difference in the thermometers. As veratric acid is $C_6H_3(OCH_3)_2COOH$, it follows that the more acid hydroxyl in curcumine is the one in the vanillin part of the molecule, that is, the one attached to the benzene ring.

Formation of Monomethylrosocyanine, $C_{14}H_{13}CH_3O_4$.—One gram of the monomethyl ether of curcumine was dissolved in a mixture of 10 grams of absolute alcohol, 0.5 gram of strong sulphuric acid, and 0.5 gram of boric acid. A crimson color appeared a few seconds after the materials were mixed, but to complete the reaction the solution was heated for half an hour on the steam bath. The intense crimson solution obtained in this way was poured into a large excess of water, which precipitated a powder looking like rosocyanine. This was washed, dried, and extracted with ether as long as a colored extract was formed, to remove unchanged monomethylcurcumine, after which it was dried for analysis.

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[1] Ann. Chem. (Liebig), **158**, 282 (1871).

[2] Gazz. chim. ital., **1876**, 142.

Monats. Chem., **6**, 378 (1887).

0.0837 gram substance gave 0.2124 gram CO_2 and 0.0510 gram H_2O.

	Calculated for $C_{15}H_{16}O_4$.	Found.
C	69.23	69.21
H	6.15	6.77

Properties of Monomethylrosocyanine.—It forms a purple powder with a metallic yellowish green reflex, looking much like rosocyanine, and is soluble in alcohol, acetone, or glacial acetic acid with a crimson color, not so brilliant as that obtained with rosocyanine; nearly insoluble in ether; and insoluble in benzene, ligroin, or water. Strong sulphuric acid dissolves it with a beautiful red color, changing slowly to brown; strong nitric acid gives a brownish yellow color, changing slowly to yellow; strong hydrochloric acid dissolves it slightly with a red color. Alkalies at first have no effect either in dissolving it or changing its color, but on long standing, caustic alkalies give a red solution, apparently of a salt of monomethylcurcumine. This behavior is what would be expected, as from our study of rosocyanine it is evident that its monomethyl ether can contain no free hydroxyl.

Application of the Rosocyanine Reaction to some other Derivatives of Curcumine.

Protocurcumine is the name we propose for the substance formed by removing one methyl group from curcumine. Its formula is $C_6H_3(OH)_2C_7H_7O_2$, and it stands in the same relation to curcumine that protocatechuic acid does to vanillic acid. This substance, which will be described in detail in a later paper, gave with boric acid, sulphuric acid, and alcohol, a crimson solution, turned blue by an alkali. On the other hand, the dimethyl ether, or the dihydride of curcumine, gave no visible reaction when warmed with boric acid, sulphuric acid, and alcohol. The significance of the experiments with these substances has been discussed in the introduction to this paper.

The investigation of rosocyanine will be continued by us in several directions, but must be preceded by the determination of the constitution of curcumine, toward which we have made good progress.

CAMBRIDGE,
January 2, 1908.

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

STUDIES IN CATALYSIS.

VI.[1] THE CATALYSIS OF IMIDOESTERS.[2]

BY HERMANN I. SCHLESINGER.

PART I.

The Velocity of Saponification of the Alkyl Imidobenzoates in the Presence of Acids, and Their Degree of Ionization.

In the well-known catalysis of ordinary acid esters by means of acids, according to the equation

$$RCOOR' + HOH = RCOOH + HOR' \qquad (1),$$

the "catalytic" functions of the acid are considered by Stieglitz[3] to consist simply in the formation of a salt of the ester and, thereby, in the increase of the concentration of the positive ion, which is considered to constitute the "active mass" of the ester. This increase, on account of the small original ionization of the ester, is directly proportional to the salt formed and, hence, to the acid used in the reaction. For the experimental investigation of the correctness of this theory, the closely related group of imidoesters, RC(NH)OR′, was employed, since for these substances the requisite experimental and mathematical data could be obtained. These esters form well defined salts with acids; the rate of their decomposition with water, according to the equation

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[1] Articles I.-V., THIS JOURNAL, **39**, 29, 166, 402, 437, 586.

[2] This article was accepted as a dissertation in July, 1905, and sent to the editor in September, 1907.

[3] Report of the Congress of Arts and Science, **4**, 278 (1904); THIS JOURNAL, **39**, 29 (1908).

$$RC(:NH)OR' + HOH = RCOOR' + NH_3 \qquad (2),$$

is accelerated considerably by the addition of an acid. The investigations carried out in this laboratory by Derby and McCracken[1] showed that, as a matter of fact, the velocity of decomposition of the imidoesters in this direction is directly proportional to the concentration of the imidoester salt present at any moment. As the experiments were carried out in dilute solutions (one-tenth to one-fortieth molar) in which the salts are almost completely ionized, the conclusion was drawn that the "active mass" of the imidoester would almost surely prove to be, not the total salt concentration, but only the ionized portion of the salt. With the purpose of testing rigorously this important point in the conclusion, the following investigation of the relation between the velocity of saponification of the hydrochlorides of the alkyl imidobenzoates and their respective degree of ionization was undertaken by me at the suggestion of Professor Stieglitz and carried out under his direction. The results obtained, in solutions varying from half molar to twentieth molar, not only showed the correctness of the conclusion that the substance reacting with water according to (2) to give an acid ester and ammonia actually is the positive ion of the salt, but, further, brought to notice another most striking parallelism in the behavior of the imidoesters and ordinary esters towards water. As is well known, the catalysis of the esters, as well as of cane sugar and similar substances, is increased by the presence of neutral salts, which produce the so-called "salt effect" studied by Spohr,[2] Arrhenius,[3] Euler,[4] and others. This "salt effect" was found by these investigators to be proportionate to the concentration of the salt added, except in the case of very dilute solutions. The results obtained by me indicate that the "catalysis" of imidoester salts is subject to exactly the same kind of "salt effect," except that, in this case, the salts involved in the reaction, *viz.*, the salt of the imidoesters and the ammonium chloride formed in the decomposition, themselves produce the acceleration—an "auto effect," as it might be called.

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[1] *Loc. cit.*

[2] J. prakt. Chem. [2], **33**, 270.

[3] Z. physik. Chem., **4**, 226 (1889).

[4] *Ibid.*, **32**, 348 (1900).

The "salt effect" is produced most markedly on substances which are but little ionized,[1] and the change in the speed of a catalysis in which water is primarily involved is ascribed particularly to the increase in the "active mass" or the dissociation of water itself in the presence of salts.[2] This explanation would account perfectly also for the "salt effect" in the decomposition of the imidoester salts—since the active mass of the water is one of the factors in the velocity formula (see equation 2).

In view of the facts established, then, since the decomposition of an imidoester into an ordinary ester is proportional to the concentration of the positive ion, the correct equation for this reaction becomes

$$C_6H_5C(:\overset{+}{N}H_2)OCH_3 + HOH = C_6H_5COOCH_3 + \overset{+}{N}H_4 \quad (2').$$

That the analogy between the ordinary esters and the imidoesters is practically complete will be shown in Part II. by proving that the imidoesters are decomposed also by means of alkalis into nitriles and alcohols, with a velocity directly proportional to the concentration of hydroxyl ion—exactly as is the case in the saponification of esters.[3]

[1] Arrhenius: *Loc. cit.*

[2] Euler: *Loc. cit.*

[3] By the action of absolute alcohols on imidoester salts Reitter and Hess (Ber. d. chem. Ges., 40, 3020) obtained ortho acid esters:

$$CH_3C(:NH_2Cl)OC_2H_5 + 2HOC_2H_5 \longrightarrow CH_3C(OC_2H_5)_3 + NH_4Cl.$$

The difference in the result of this action and that of water on such salts suggested that the formation of ortho esters would be found due to the following sequence of reactions:

$$CH_3C(:\overset{+}{N}H_2)OC_2H_5 + HOC_2H_5 \longrightarrow CH_3C(\overset{+}{N}H_3)(OC_2H_5)_2 \longrightarrow CH_2:C(OC_2H_5)_2 + \overset{+}{N}H_4;$$

and $$CH_2:C(OC_2H_5)_2 + HOC_2H_5 \longrightarrow CH_3C(OC_2H_5)_3.$$

As a matter of fact Reitter has isolated, in the case of cyanacetic ester, a compound $C(OC_2H_5)_2:CH.CO_2C_2H_5$ (*loc. cit.*, 40, 3358), either as an intermediate or a final

EXPERIMENTAL.

1. The Hydrochloride of Ethyl Imidobenzoate.

The velocity of the decomposition by water of the hydrochloride of ethyl imidobenzoate, according to the equation

$$C_6H_5C(:\overset{+}{N}H_2)OC_2H_5 + H_2O = C_6H_5COOC_2H_5 + \overset{+}{N}H_4 \quad (3),$$

was determined at 25°, in solutions containing one mole in 2, 4, 5, 10, and 20 liters, respectively. The solutions were placed in a bath of 320 liters capacity, whose temperature was kept at 25° (±0.01) by means of an Ostwald thermostat. The method of analysis used was the one described by Derby:[1] by means of a pipette, a measured portion (25, 10, or 5 cc.) of the salt solution was rapidly run into a known amount of standard sodium hydroxide solution (an excess of this was used); the free imidoester liberated was removed by three extractions with carbon tetrachloride (15, 10, and 5 cc., respectively); and the excess of sodium hydroxide in the aqueous residue determined by titration with standard hydrochloric acid. Methyl orange was used as indicator.

A mixture of a benzimidoester hydrochloride and ammonium chloride behaves under this treatment exactly as does a mixture of free hydrochloric acid and ammonium chloride; the imidoester salt neutralizes part of the added alkali, while

product. On the basis of this hypothesis of an *intermediate* product, the reaction would not work with the imidoester salts of a tertiary acid, like benzimidoesters, and a reply of Professor Reitter to a private inquiry has confirmed the correctness of this surmise, as far as preliminary experiments go. Professor Reitter, with Dr. Hess, has kindly consented to our taking up this part of the problem as well as the physicochemical study of the formation of ortho esters, while he and his collaborators will develop it from the preparative side and endeavor to isolate the compounds $C_6H_5CH:C(OR)_2$ in the action of alcohols on the imidoester salts of benzyl cyanide. These facts are mentioned here because the work on saponification and esterification, etc., is being taken up by us along these lines with aliphatic esters and imidoesters of primary, secondary, and tertiary acids, *as such reactions may form parallel or even the main intermediate actions* in some cases of ordinary saponification, etc. It may be recalled that McCracken and I have already found that the velocity of decomposition of imidoester salts of phenylacetic acid is exceedingly high, very much higher than that of aromatic salts, and it should be said that Dr. Blunt has obtained a similar result for the action of ammonia on such salts. These and a large number of other facts recorded by different investigators, (Cf. Nef, Standinger, Wilsmore) which will be discussed at the proper time, promise to lead to a deeper insight into all the various sides of these problems than has hitherto been obtained.—JULIUS STIEGLITZ (May, 1908).

[1] THIS JOURNAL, **39**, 437 (1908)

this is not true in the case of ammonium chloride; unlike the free imidoester, ammonia in very dilute solution is not appreciably removed by carbon tetrachloride, and hence, since methyl orange is sensitive to it as well as to the fixed alkali, it does not affect the titration. Thus, if b cc. of N/10 sodium hydroxide are added to v cc. of the salt solution and d cc. of N/10 hydrochloric acid are required after the extractions to neutralize the excess of alkali, the concentration of the unchanged salt is proportional to $(b-d):v$. The observed values given below were obtained in this way.

The velocity constants were calculated according to the equation for a monomolecular reaction,

$$\frac{dx}{dt} = K_v(C - x) \qquad (4),$$

and

$$K = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (5).$$

As Derby[1] has shown, the substance undergoing change is the salt or its positive ion alone, and not the free base liberated by the hydrolytic action of the water present. Inasmuch as the degree of hydrolysis is less than one per cent for ordinary dilutions, the free base liberated is a negligible quantity and the salt may be put equal to the total quantity of unchanged substance.

For each concentration for which the velocity was determined, the degree of ionization of the salt was found experimentally. This value, in a given experiment with given concentration of salt, may be considered a constant for the experiment; although the imidoester salt used is growing smaller in concentration during the course of the reaction, each molecule is being replaced by one of ammonium chloride, and the total electrolytic content in this way remains unchanged. Under these conditions, according to the laws of isohydric solutions, the degree of ionization of the imidoester salt may be considered practically a constant for the whole period of a velocity determination. The value of the ionization factor will be incorporated in the final velocity constant in the manner discussed below (p. 729); for each determination the velocity constant, independent of the ionization, will, however, first be calculated simply according to equation (5).

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[1] *Loc. cit.*

In the following tables, v gives the volume in liters containing one gram molecule of the imidoester salt, w gives the portion in cc. used for each titration at the time indicated under t. This line contains the time in minutes, from the time of the first titration to the moment when the first quantity (w) of solution was introduced into the excess of alkali; in line 2, under ($C—x$), will be found the cc. of N/10 alkali neutralized by the unchanged imidoester salt contained in the w cc. used for the titration. The concentration of the unchanged substance, ($C—x_1$), etc., is proportional to this value. In line 3, the velocity constants calculated according to equation (5) are given, the values being 43430 times the true constant. All the determinations were made, as mentioned, at 15° (±0.01).

As was anticipated, the tables show that the velocity of decomposition is very markedly dependent on the concentration of the salt used. To determine rigorously whether this result is due to the fact that only the positive ion of the salt is reacting and not the nonionized molecule, the degree of dissociation of the hydrochloride of ethyl imidobenzoate in the various concentrations used was determined by the conductivity method. Owing to the fact that the salt is very rapidly decomposed by water at 25°, the conductivity measurements were made at 0°; at this temperature, much less difficulty was experienced in obtaining satisfactory results, since the rate of decomposition is slow. The work of H. C. Jones[1] on the degree of ionization of chlorides shows that this value is practically the same at 0° as at 25°; hence the values obtained at 0° for the hydrochloride used may be employed to calculate the relations desired at 25°. On account of the hydrolytic dissociation of the hydrochloride according to the equation

$$C_6H_5C(NH_2Cl)OC_2H_5 \rightleftarrows C_6H_5C(NH)OC_2H_5 + HCl \qquad (6),$$

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[1] THIS JOURNAL, **26**, 1442 (1901).

The Hydrochloride of Ethyl Imidobenzoate.

Table Ia.

$v = 20.$ $w = 25$ cc. Mean, 43430 $K_v = 136.$

t	0	60	90	120	150	180	210
$(C—x)$	11.77	9.75	8.93	8.10	7.35	6.73	6.04
43430 K_v	....	136	133	135	136	135	138

Table Ib.

$v = 20.$ $w = 25$ cc. Mean, 43430 $K_v = 135.$

t	0	30	60	90	180	210	240
$(C—x)$	12.01	10.97	9.98	9.09	6.79	6.11	5.18
43430 K	....	131	134	134	137	140	135

Table IIa.

$v = 10.$ $w = 10$ cc. Mean, 43430 $K_v = 132.$

t	0	30	60	90	120	150	286	315	375
$(C—x)$	9.60	8.74	8.03	7.35	6.64	6.04	4.13	3.69	3.10
43430 K_v	....	136	129	129	134	135	128	132	132

Table IIb.

$v = 10.$ $w = 10$ cc. Mean, 43430 $K_v = 133.$

t	0	30	60	90	120	150	240	270	300
$(C—x)$	9.75	8.89	7.98	7.35	6.67	6.20	4.70	4.32	3.87
43430 K_v	....	134	(145)	136	136	131	132	131	134

The Hydrochloride of Ethyl Imidobenzoate.

Table IIIa.

$v = 5$. $w = 10$ cc. Mean, $43430\ K_v = 122$.

t	0	30	60	90	120	240	285	330
$(C-x)$	19.24	17.57	16.24	15.04	13.61	9.84	8.57	7.55
$43430\ K_v$	....	(131)[1]	123	119	125	121	123	123

Table IIIb.[2]

$v = 5$. $w = 5$ cc. Mean, $43430\ K_v = 126$.

t	0	30	60	90	120	153	180	210
$(C-x)$	9.61	8.74	8.05	7.41	6.79	6.14	5.79	5.17
$43430\ K_v$	....	(137)	128	125	126	127	122	128

Table IIIc.

$v = 5$. $w = 10$ cc. Mean, $43430\ K_v = 121$.

t	0	25	55	85	115	145	236	265
$(C-x)$	19.15	17.79	16.48	15.09	13.95	12.77	9.82	9.27
$43430\ K_v$	....	(128)	119	122	120	121	123	119

Table IVa.

$v = 4$. $w = 10$ cc. Mean, $43430\ K_v = 120$.

t	0	45	75	105	210	240	270	300	345
$(C-x)$	24.27	21.22	19.71	18.17	13.59	12.64	11.47	10.71	9.59
$43430\ K_v$	....	(130)	120	120	119	120	121	119	123

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[1] The first titrations at the end of 25 to 30 minutes often gave an abnormal constant, high or low, probably due chiefly to the fact that a small difference in the titration, $(C-x)$, produces a large difference in the value K_v.

[2] The temperature of the bath during this determination was about 0.03° too high. This probably accounts for the high value of K_v.

The Hydrochloride of Ethyl Imidobenzoate.

Table IVb.

$v = 4$. $w = 10$ cc. Mean, $43430\ K_v = 119$.

t	0	30	60	90	121	255	285	316	345
$(C-x)$	24.17	22.44	20.50	18.94	17.36	12.12	11.19	10.06	9.43
$43430\ K_v$	....	(107)	119	118	119	118	117	120	119

Table Va.

$v = 2$. $w = 5$ cc. Mean, $43430\ K_v = 107$.

t	0	30.2	60	90	241	270	300	330
$(C-x)$	22.89	21.24	19.89	18.26	12.86	11.86	10.90	10.00
$43430\ K_v$		108	103	109	104	106	107	109

Table Vb.

$v = 2$. $w = 5$ cc. Mean, $43430\ K_v = 105$.

t	0	29	59	89	119	244	269	299	332
$(C-x)$	24.33	22.74	21.21	19.78	18.15	13.67	13.03	11.95	11.09
$43430\ K_v$	....	101	101	103	107	104	105	107	106

it was necessary to determine the conductivity by Bredig's method[1] in the presence of an excess of the free base sufficiently great to neutralize the acid liberated and small enough to have no appreciable conductivity of its own in the presence of its salt. Because of the instability of the salt in aqueous solution, the following methods of operation were used: In the case of the more concentrated solutions (N/10–N/2) a small cell of the Kohlrausch type was employed. The cell had a capacity of about 4 cc.; the electrodes, whose diameter was about 7 mm., were, when fully immersed, separated by a column of liquid about 35 mm. in length and 5 mm. in diameter. Solutions of the free base of the approximate concentrations, N/40 and N/80, were made up and kept at —5°. The salt was weighed out into a dry graduated 5 cc. flask, the flask filled with one or the other of the free base solutions, and the whole well mixed and cooled to zero; the mixture was then poured rapidly into the small cell, which was kept in a zero bath, and the resistance of the solution measured by means of a Kohlrausch bridge and telephone. In the case of the more dilute solutions (N/20–N/256), an ordinary Arrhenius cell was used. The solutions of free base were kept in 50 cc. flasks calibrated for delivery; the salt was weighed out in a small beaker, the solution of free base poured over it from the graduated flask, and the whole well mixed and cooled to about —0°.5. This solution was then poured into the Arrhenius cell and its resistance measured in the usual way. In all the experiments, a calibrated thermometer was used, and the resistance measured at exactly 0°. It was found that the resistance remained constant for longer than 10 minutes, thus showing that no appreciable decomposition had set in.

In Table VI., the results obtained for the conductivities are given. Column 1 contains the volume in which one gram molecule of salt is dissolved; in columns 2 and 5 the molecular conductivities (Λ_v) in the presence of an excess of one-eightieth and one-fortieth normal free base, respectively, will be found; in column 3 are given the differences (Δ) which must be added to the molecular conductivities (Λ_v) to obtain the conductivity (Λ_∞) for the salt at infinite dilution. According to Ostwald[1] and Bredig,[2] these differences are considered to have a fairly constant value for the various classes of salts in solutions varying in concentration from N/1024 to lower concentrations. The differences (Δ) used in the following table were calculated from Bredig's values[3] by multiplication, first by the factor 1.065 to reduce reciprocal mercury units to reciprocal ohms, and second, by the factor 0.45, which is the approximate correction (within two or three per cent) for the change of temperature from 25° to 0°.[4] Briefly,

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[1] Z. physik. Chem., **13**, 213 (1894).

$$\Delta_0 = \Delta_{25^\circ} \times 1.065 \times 0.45.$$

In columns 4 and 6 we have placed the molecular conductivities at infinite dilution (Λ_∞) as calculated from Δ_v and Λ_v. In column 7, the degree of ionization (α_v) of the salt is given for each concentration.

Ethyl Imidobenzoate Hydrochloride.

Table VI.

1	2	3	4	5	6	7
V.	Λ_v.[5]	Δ.	Λ_∞.[8]	Λ_v.[6]	Λ_∞.	$\alpha_v \times 100$.
2	30.6	....	....	30.5	....	56.6
4	37.0	....	....	37.0	....	68.5
5	38.7	....	....	38.7	....	71.7
10	43.6	....	....	43.6	....	80.7
20	....	7.7[7]	....	45.7	53.4	84.6
32	47.0	6.7	53.7	47.3	54.0	87.3
64	48.7	5.3	54.0	49.1	54.4	91.0
128	50.4	3.8	54.2	50.4	54.2	93.3
		Mean,	54.0	Mean,	54.0	

If the observed velocity constants, K_v (column 3, Table IV.) for the decomposition of the hydrochloride of ethyl imidobenzoate in varying concentrations be divided by the corresponding degree of ionization,[1] we obtain as the *apparent* velocity of decomposition of the positive ion,

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[1] Z. physik. Chem., **2,** 840.

[2] *Ibid.,* **13,** 198 (1894).

[3] *Loc. cit.*

[4] Stieglitz and Upson: THIS JOURNAL, **31,** 469 (1904).

[5] These are the values for Λv when an excess of N/80 base was used.

[6] These are the values for Λv when an excess of N/40 base was used.

[7] Found by extrapolation.

[8] This column contains the values of Λ_∞ calculated from Λv in column 2; those calculated from Λv in column 5 will be found in column 6.

$$K_{ion\ app.} = \frac{K_v}{\alpha_v} \qquad (7).$$

This gives a series of values representing the velocity constants (column 4, Table VII.), calculated on the assumption that only the positive ion of the salt is undergoing decomposition by water. As is well known, however, the speed of reactions in which water is an active agent is greatly accelerated by the presence of neutral salts.[2] This effect may be due to an increase, by the salt, in the active mass of the water;[3] but, whatever the cause, the fact remains that neutral salts have this influence and that, except for extreme dilutions, the effect is fairly proportional to the concentrations of the salt used. As a general rule, it is true also that there is comparatively little difference in the effect of analogous inorganic salts.[4] In order, in our case, to determine this "salt effect" and find the true velocity of decomposition of the positive ion, K_{ion}, when, hypothetically, there is no salt present and hence no "salt effect," we may consider the apparent velocities, $K_{ion\ app.}$ (given in Table VII., column 4), for 0.05, 0.1, and 0.20 molar solutions, respectively. Inspection shows at once that the "salt effect" for every 0.05 mole salt may be taken to be 3 in the terms of the same units as are used for K. Then for the hypothetical case, where the salt concentration is 0, we would have, since here there is no "salt effect,"

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[1] In the decomposition of the imidoester salt, ammonium chloride replaces the hydrochloride of the imidoester. According to the laws of isohydric solutions, however, the degree of ionization of the unchanged imidoester salt will remain practically unaltered, since the total electrolyte content remains constant. The somewhat greater degree of ionization of ammonium chloride will have a negligible effect.

[2] Part I., page 720.

[3] Euler: Z. physik. Chem., **32**, 348 (1900).

[4] Arrhenius: *Loc. cit.* This may explain why the change of the imidoester salt into ammonium chloride does not seem to change the "salt effect" to any great extent. In Tables I.–V. K_v does not change much in the six hours during which velocities were measured. It is peculiar, however, that the "auto effect" of the hydrochloride of methyl imidobenzoate seems to be twice as great as for the hydrochloride of ethyl imidobenzoate. A thorough investigation of the effect of different salts is being carried out by Miss Edith E. Barnard.

NOTE.—Miss Barnard's work has now been completed. A more reliable method of determining Λ_∞, and consequently the degrees of ionization, employed by us has given very accurate results, confirming the fact that the salt effect is proportionate to the ion concentrations, and that the velocity of decomposition is otherwise proportionate to the ionized part of imidoester salts.—J. STIEGLITZ.

$$K_{ion} = 161—3;$$
$$K_{ion} = 158 \qquad (8).$$

From this we see that the "salt effect" consists in an acceleration of the velocity of 3/158, or practically 2 per cent for every 0.05 gram molecule of salt present. Considering the effect as proportional to the total salt present, we may write

$$K_{ion\ app.} = K_{ion} \times \left(1 + \frac{m}{0.05} \times 0.02\right) = 158 \times \left(1 + \frac{m}{0.05} \times 0.02\right) \qquad (9).$$

Combining equations (7), (8), and (9), we find that we can calculate the velocity with which the hydrochloride of ethyl imidobenzoate should be decomposed by water at any concentration. The following equation expresses the relationship:

$$K_{calc.} = K_{ion} \times \alpha_v \times \left(1 + \frac{m \times 0.02}{0.05}\right) \qquad (10),$$

$$= 158 \times \alpha_v \times \left(1 + \frac{m \times 0.02}{0.05}\right) \qquad (10').$$

In this equation, m is the concentration of the imidoester salt in gram molecules per liter and α_v is the degree of ionization. The values for $K_{calc.}$ are found in column 5, Table VII.

It is very likely, however, that the true "salt effect" is essentially due to the ionized part of the salt present and not to the total salt;[1] under these circumstances, the following equation should more correctly represent the facts:

$$K_{calc.} = K_{ion} \times \alpha_v \times \left(1 + \frac{m \times 0.02 \times \alpha_v}{0.05 \times \alpha_{0.05}}\right) \qquad (11),$$

$$= 158 \times \alpha_v \times \left(1 + \frac{m \times 0.02 \times \alpha_v}{0.05 \times 0.846}\right) \qquad (11').$$

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[1] Arrhenius: *Loc. cit.* Euler: *Loc. cit.*

The values calculated in this way are found in the last column of Table VII. It is obvious that a striking agreement exists between the theoretical velocities calculated according to either equation (10′) ($K_{calc.}$ in column 5) or equation (11′) ($K'_{calc.}$ in column 6) and the velocities actually observed (K_v in column 3). The greatest deviation, in fact, from the theoretical values is 3.5 per cent., which is well within the limits of experimental errors.

Table VII.

1 m.	2 100 α_v.	3 43430 K_v.	4 43430 $\times \frac{K_v}{\alpha_v}$.	5 43430 $\times K'_{calc.}$	6 43430 $\times K_{calc.}$
0.50	56.6	105	185.5	107	101.5
0.25	68.5	120	175	119	117
0.20	71.7	121.5	169.5	122.5	121
0.10	80.7	132.5	164	132.5	132
0.05	84.6	136	161	136	136
0.00	....	....	158[1]	....	....

The "salt effect" may be represented graphically in the following diagram, in which the velocity constant $K_v : \alpha_v$, with no correction for the "salt effect" (column 4), is given on the horizontal coördinate, and the total concentration of ionized salt is given on the ordinate ($C_{ions} = m \times \alpha$). The curve represents an almost straight line, showing an acceleration directly proportional to the concentration of the ionized salt present.

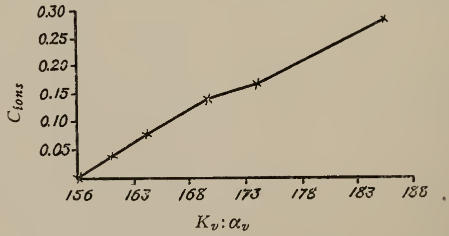

Fig. 1.—Ethyl Imidobenzoate.

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[1] This value is hypothetical.

Judging by these results, we would decide that the decomposition of the hydrochloride of ethyl imidobenzoate by water proceeds with a velocity proportional to the concentration of the positive ion of the salt, and this velocity is accelerated by the influence of a "salt effect" which is proportionate to the concentration of the salt ions present.[1] This result is in perfect agreement with Stieglitz's theory of the catalysis of esters.

2. *The Hydrochloride of Methyl Imidobenzoate.*

In order to test the theory more fully, a series of experiments, exactly similar to those performed with the hydrochloride of ethyl imidobenzoate, was carried out with the corresponding salt of methyl imidobenzoate. The tables and the symbols employed correspond to those in the preceding part of the paper, as do also all the experimental details; no further discussion, therefore, is required.

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[1] This conclusion has been confirmed by the extended investigations of Dr. Barnard.

The Hydrochloride of Methyl Imidobenzoate.

Table VIIIa.

$v = 20.$ $w = 25$ cc. Mean, $43430\,K_v = 236.$

t	0	30	60	90	120	150	255	285	315
$(C—x)$	10.93	9.40	7.63	6.72	5.71	4.81	2.80	2.61	1.85
$43430\,K_v$	....	218	260	234	235	237	230	218	257

Table VIIIb.

$v = 20.$ $w = 25$ cc. Mean, $43430\,K_v = 235.$

t	0	30	60	90	120	225	255	285
$C(—x)$	8.10	6.90	5.67	5.51	4.35	2.39	2.07	1.85
$43430\,K_v$	.....	232	258	(186)	225	235	233	225

Table IXa.

$v = 10.$ $w = 10$ cc. Mean, $43430\,K_v = 242.$

t	0	30	60	90	120	150	270	300	330
$(C—x)$	9.38	7.96	6.47	5.75	4.88	3.99	2.20	1.75	1.5
$43430\,K_v$	....	238	(269)	236	237	247	233	243	236

The Hydrochloride of Methyl Imidobenzoate.

Table IXb.

$v = 10.$ $w = 10$ cc. Mean, $43430\,K_v = 246.$

t	0	30	60	90	120	150	271	301	330
$(C-x)$	9.47	7.75	6.37	5.85	4.79	4.18	2.10	1.82	1.50
$43430\,K_v$	....	(290)	(287)	233	247	236	235	283	241

Table Xa.

$v = 5.$ $w = 10$ cc. Mean, $43430\,K_v = 234.$

t	0	30	60	90	120	210	240	255
$(C-x)$	16.46	13.95	11.97	9.81	7.93	5.43	4.61	4.23
$43430\,K_v$	....	239	231	(249)	(264)	230	236	237

Table Xb.

$v = 5.$ $w = 10$ cc. Mean, $43430\,K_v = 231.$

t	0	30	60	90	150	240	270	315
$(C-x)$	18.50	15.96	13.30	11.45	8.27	5.40	4.49	3.56
$43430\,K_v$	....	(214)	239	232	231	224	228	227

The Hydrochloride of Methyl Imidobenzoate.

Table XI.

$v = 4.$ $w = 5$ cc. Mean, $43430\ K_v = 230.$

t	0	30	60	90	255	270	285	300	315
$(C-x)$	12.24	10.43	8.85	7.59	3.13	2.99	2.70	2.53	2.36
$43430\ K_v$	....	232	235	231	232	227	231	228	227

Table XIIa.

$v = 2.$ $w = 5$ cc. Mean, $43430\ K_v = 207.$

t	0	30	60	75	120	150	270	300	330
$(C-x)$	23.37	20.33	17.61	15.75	13.29	11.20	6.47	5.50	4.85
$43430\ K_v$	....	202	205	(222)	205	(213)	207	207	207

Table XIIb.

$v = 2.$ $w = 5$ cc. Mean, $43430\ K_v = 208.$

t	0	30	60	105	120	150	300	330
$C-x$	23.89	20.70	17.66	14.46	13.43	11.32	5.76	4.99
$43430\ K_v$	....	208	(218)	208	209	(216)	206	206

Table XIII.[1]—*The Degree of Ionization of the Hydrochloride of Methyl Imidobenzoate.*

1	2	3	4	5	6	7
$V.$	$\Lambda v.$[2]	$\Delta.$	$\Lambda\infty.$[2]	$\Lambda v.$[3]	$\Lambda\infty.$[3]	$\alpha v \times 100.$
2	31.6	....	....	32.9	....	58.5
4	38.5	....	....	38.6	....	70.0
5	40.1	....	....	39.8	....	72.5
10	43.8	....	....	44.7	....	80.3
32	48.2	6.7	54.9	48.2	54.9	87.5
64	50.1	5.3	55.4	49.9	55.1	90.7
128	51.8	3.8	55.6	50.7	54.5	92.5
		Mean,	55.3	Mean,	54.9	

Average $\Lambda\infty = 55.1.$

Table XIV.[4]

1	2	3	4	5	6
$m.$	$100\,\alpha v.$	$43430\,K_v.$	$43430\frac{K_v}{\alpha v}.$	$43430\,K_{calc.}$	$43430\,K'_{calc.}$
0.50	58.5	207	354	225	206
0.25	70.0	230	328	231	225
0.20	72.5	232	320	231	227
0.10	80.3	244	304	238	237
0.05	84.6[5]	236	279	242	242
0.05	84.6	242[6]	286[7]	242	242
0.00	....	...	275[7]	...	...

The values in the table above (Table XIV.) give the relations of the velocity of decomposition of the hydrochloride of the methyl imidobenzoate (as taken from Tables VIII.–XIII.) to the degree of ionization of the salt and to the "salt effect" in any concentration. In Table XIV., as in Table VII., column 3 gives the velocities actually observed (K_v), and in columns 5 and 6 the theoretical velocity constants as calculated by equations analogous to (10′) and (11′), respectively, are given;[1] into this last column "salt effect" and degree of ionization are both incorporated. It is noticeable at once that the calculated values ($K'_{calc.}$) for an accelerating effect of the salt *ions* agree remarkably well (within 2–3 per cent) with the observed velocities (K_v). As was expected, the values calculated for an accelerating effect proportional to the total salt ($K_{calc.}$) do not agree so well with the observed velocities—the maximum deviation being as high as 8.8 per cent in one case. In both cases, therefore, for the hydrochlorides of methyl as well as of ethyl imidobenzoate, the agreement between the velocities calculated on the basis of an equation like (11′) agree well with the observed velocities. We may consider then that such an equation actually gives the best expression of the course of the reaction according to which an imidoester salt is decomposed into an ester and an ammonium salt (equation 2′).[2]

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[1] Tables XIII. and XIV. are comparable to Tables VI. and VII., respectively.

[2] Column 2 contains Λv when N/80 base was used in excess. In column 4 the Λ_∞ was calculated from Λv in column 2.

[3] Column 5 contains Λv when N/40 base was used in excess; column 6, the corresponding Λ_∞.

[4] Tables XIII. and XIV. are comparable to Tables VI. and VII., respectively.

[5] Taken from the ethyl ester. See Table VI., column 7.

[6] Taken from the work of Derby: *Loc. cit.* Mean of 23 determinations.

[7] The acceleration due to salt is taken from these two values. It is $\frac{11.1}{275} = 0.04$ for 0.05 mole of salt.

PART II.

The Catalysis of Imidoesters by Means of the Hydroxyl Ion.

A qualitative investigation of the action of alkalis on imidoesters of the aromatic series showed that the reaction proceeds in a direction different from that exhibited in acid solution; instead of an ester and an ammonium salt (equation 2′), a nitrile and an alcohol are formed according to the equation

$$C_6H_5C(:NH)OR = C_6H_5C \equiv N + HOR \qquad (12).$$

This, it should be noted, is a reversal of the synthetic method of preparing imidoesters from nitriles and alcohols in the presence of acids.

The quantitative determinations of the velocity of decomposition, under the influence of varying proportions of barium hydoxide, show that the velocity is always directly proportional to the concentration of the imidoester and to the concentration of the hydroxyl ion, *i. e.*,

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[1] The acceleration is taken as 4 per cent for 0.05 mole salt.

[2] Work is being continued along these lines by Mr. W. Hickman, velocities being measured at 0° as well as at 25°.—J. S.

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times C_{OH} \qquad (13).^1$$

The hydroxyl ion may be said to act "catalytically," in the old sense of the term, as it does not appear to be involved in the reaction and its concentration remains constant. This is true because both the original imidoester used and the alcohol formed are too weak acids to neutralize appreciably the alkali in the dilute solutions used. For a given experiment, therefore, we may write

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times k_{OH} \qquad (14),$$

$$= K_v \times C_{ester} \qquad (14').^1$$

Or

$$\frac{dx}{dt} = K_v \times (C - x) \text{ and}$$

$$K_v = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (15).$$

The velocity constant of the decomposition, K_{OH}, is, according to (14) and (14′),

$$K_{OH} = \frac{K_v}{k_{OH}} \qquad (16),$$

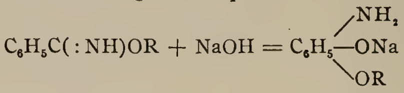
in which k_{OH} is the given concentration of the hydroxyl ion used in an experiment and K_v is the observed velocity constant in that experiment. If the decomposition actually proceeds according to (13), the same value for K_{OH} ought to be obtained from all the determinations, independent of the concentration of the imidoester and of the barium hydroxide used. The results reported below fully prove that such is the case.

According to the theory developed in Stieglitz's paper,[2] the enormous acceleration of the decomposition of imidoesters into alcohols and nitriles produced by alkalis as catalytic agents must be due to acid properties of the imidoesters. Such a character would lead to the formation of metal salts

[1] C_{ester} is a function of x.

[2] *Loc. cit.*

whose *negative ion* would be the actual substance undergoing decomposition and the concentration of whose negative ion would constantly represent the real "active mass" at any moment. The imidoesters, consequently, must have an amphoteric character, ionizing chiefly as bases, yet minimally also as acids, and forming salts with the alkalis. There are two ways in which such a salt formation could occur; either by direct addition of alkali to the imidoester, just as to an ordinary ester,[1] according to the equation



$$C_6H_5C(:NH)OR + NaOH = C_6H_5\begin{cases} NH_2 \\ ONa \\ OR \end{cases} \qquad (17),$$

or by salt formation in the imido group according to the equation

$$C_6H_5C(:NH)OR + NaOH = C_6H_5C(:NNa)OR + H_2O \quad (18).$$

In view of the fact that the very closely related class of bodies, the amidines, $RC(:NH)NH_2$, besides their pronounced basic properties—they are far stronger bases than the imido esters, even stronger than ammonia—have been shown to possess also weak acid properties, forming salts such as $RC(:NMe)NH_2$[2] and $RC(:NC_6H_5)(NMeC_6H_5)$,[3] it is extremely probable that equation (18) represents the actual method of salt formation.[4] For the further development of our theory, it is a matter of indifference whether (17) or (18) is correct, but (18) gives a rather more simple decomposition of the imidoester into nitrile and alcohol than does (17), from which one would expect the formation of an alcohol and an acid amide, $RCONH_2$.

The salts of very weak acids, as the imidoesters must be, are hydrolyzed in aqueous solutions according to the formulation

$$C_6H_5C(:NMe)OR + HOH \rightleftarrows C_6H_5(:NH)OR + MeOH \qquad (19),$$

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[1] Claissen: Ber. d. chem. Ges., **20,** 641 (1887); Nef: Ann. Chem. (Liebig), **270,** 322; **287,** 279.

[2] Bruce: J. Am. Chem. Soc., **26,** 419 (1904).

[3] Bamberger: Ann. Chem. (Liebig), **273,** 277 (1893).

[4] The isolation and analysis of the metal salts of the imidoesters will be attempted in this laboratory.

and we would have for the *free weak acid* (the imidoester)

$$\frac{C_{neg.\,ion} \times C_H}{C_{mol.}} = k_{acid} \qquad (20),$$

in which the $C_{neg.\,ion}$ represents the concentration, in the usual units, of the negative ion of the acid, C_H the concentration of hydrogen ions, and $C_{mol.}$ that of the nonionized acid, and k_{acid} is the affinity (ionization) constant of the imidoester as an acid. The proportion of ester which is ionized as an acid is so exceedingly small that we may consider the concentration of the nonionized ester, $C_{mol.}$, equal to the total concentration of ester, C_{ester}, at any moment and hence write

$$\frac{C_{neg.\,ion} \times C_H}{C_{ester}} = k_{acid} \qquad (20').$$

Since

$$C_H \times C_{OH} = k_{H_2O} \qquad (21),$$

we have, combining (21) and (20′),

$$\frac{C_{neg.\,ion}}{C_{ester} \times C_{OH}} = \frac{k_{acid}}{k_{H_2O}} \qquad (22).$$

If, now, according to Stieglitz's theory, the substance which is actually undergoing decomposition into a nitrile and an alcohol is the negative ion of the imidoester, in other words, if we put simply

$$\frac{dx}{dt} = K_{ion} \times C_{neg.\,ion} \qquad (23),$$[1]

then we must find the following equation, obtained by combining (23) and (22), to be true:

$$\frac{dx}{dt} = K_{ion} \times \frac{k_{acid}}{k_{H_2O}} \times C_{ester} \times C_{OH} \qquad (24),$$

$$= K_{OH} \times C_{ester} \times C_{OH} \qquad (25).$$

This expression, however, is identical with equation (13), which is, on the one hand, in perfect agreement with the experimental results; and can, on the other hand, it is seen, be deduced theoretically by the application of the well-known laws of chemical equilibrium to the fundamental conception of salt and ion formation as the explanation of the catalytic action of acids and bases.

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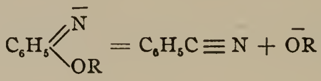
[1] $C_{neg.\,ion}$ is a function of x.

We may, therefore, properly write the decomposition reaction in alkaline solution as follows:



$$C_6H_5\Big\langle\begin{matrix}\overline{N}\\ OR\end{matrix} = C_6H_5C\equiv N + \overline{O}R \qquad (26),$$

which corresponds in every way to equation (2′) for the decomposition of the positive imidoester ions into ammonium ions and esters. In the latter case, the basic properties of the imidoesters were sufficiently strong to permit a determination of the actual concentrations of the *positive* ion and of the real constant, K_{ion}; in the case of the decomposition of the *negative* ions into nitriles and alcohols, the acid ionization of the imidoester is so slight that the determination of k_{acid} in equations (20) and (22) was not attempted, and consequently we have been unable to resolve the experimental constant K_{OH} of equation (25). But from the fact that K_{OH} has been found to be 1.991 for methyl imidobenzoate (see below), it is seen that the velocity of decomposition of the negative ion is very much larger than the velocity of decomposition of the positive ion of the same ester, whose value has been found to be 0.0063 (see p. 737, Table XIV.). There again, the imidoesters show a perfect parallelism to the ordinary esters, which are decomposed very much faster by alkalis than by acids.

EXPERIMENTAL.

The qualitative examination of the change of the imidoesters in alkaline solution was made on two representative substances, methyl imidobenzoate and methyl imido-*m*-nitrobenzoate. The experiments were carried out as follows: About one gram of the ester was weighed out into a tube of about 50 cc. capacity and to this was added a measured amount of N/10 barium hydroxide. The tube was then attached to the wheel of a small engine and shaken for ten to twenty hours. In the case of the methyl imidobenzoate, benzonitrile separated out as a heavy oil; this was filtered off, dried in a desiccator, and weighed. In order to establish its identity, a portion was dissolved in alcohol, mixed with 15 drops of concentrated ammonia solution, and treated for sixty hours with hydrogen sulphide. The resulting thiobenzamid was dissolved in dilute sodium hydrate and reprecipitated by means of carbon dioxide. This product, when dry, melted at 115°. No very accurate quantitative results were obtained in this way in the case of methyl imidobenzoate, as benzonitrile is quite soluble in water and there is another loss; it was necessary to wash the filter with a few drops of alcohol, as was done with the tube in order to obtain all of the nitrile; the alcohol was completely evaporated in the desiccator, but experiment showed that benzonitrile was also slightly volatile under these circumstances. In spite of these difficulties, 0.9 gram of methyl imidobenzoate, when treated with 25 cc. of N/10 barium hydroxide, for twelve hours, yielded 0.35 gram of benzonitrile—50 per cent of the theoretical value. In the case of methyl imido-*m*-nitrobenzoate, the nitrile, under the treatment described, separated as a white, crystalline substance. It was filtered from the solution, washed with dilute hydrochloric acid to remove any unchanged solid ester, dried on a clay plate, and weighed. The nitrile thus obtained melted sharply at 116°. The filtrate was then heated to about 80° in the presence of dilute hydrochloric acid to convert any unchanged dissolved ester into methyl *m*-nitrobenzoate and extracted with low boiling ligroin. The extract was dried with calcium chloride and allowed to evaporate spontaneously. Only a small quantity of pure *m*-nitrobenzonitrile was left. One gram of ester shaken for 20 hours with 25 cc. of N/10 barium hydroxide yielded 0.5 gram of nitrile—67 per cent of the theoretical value. It is apparent, therefore, that equation (12) represents the chief reaction.

The quantitative study of the accelerating action of hydroxyl ions on the decomposition of imidoesters into nitrile and alcohols included velocity determinations on methyl, ethyl, propyl, and isopropyl imidobenzoates and methyl imido-*m*-nitrobenzoate. The method of analysis used to follow the reaction and the conditions of the experiment will be described in detail for the first one of the series examined, methyl imidobenzoate, where special precautions had to be used.

1. Methyl Imidobenzoate.

Methyl imidobenzoate was prepared from its hydrochloride by treatment of the latter with three times the calculated amount of a cold 30 per cent solution of sodium hydroxide and rapid extraction with ether. The extract was dried with calcium chloride and the ether distilled off under diminished pressure. The remaining oil was then distilled at a pressure of 2 mm. or less.[1] At this pressure, methyl imidobenzoate (as well as ethyl, propyl, isopropyl, and isobutyl esters) distil without visibly boiling and without decomposition. In order to test the purity of the compound, it was titrated[2] with N/10 hydrochloric acid. Instead of stopping the addition of acid at the ordinary "neutral" tint, the solution was titrated to a "standard" tint prepared by adding a few drops of the indicator (methyl orange) to a N/50 solution of corresponding pure hydrochloride. The ester was diluted so as to give, when titrated, a salt solution of the same concentration as that of the standard tint. The very slight hydrolysis of the hydrochloride is by this means prevented from affecting the accuracy of the titrations.

The velocity of decomposition of the imidoesters in the presence of barium hydroxide was determined, as in the case of the hydrochlorides, at 25° (±0°.01). The required amount of N/10 barium hydroxide was run into a 500 cc. graduated flask and the solution made up to the mark. This aqueous solution was poured into an ordinary 750 cc. flask and kept, well stoppered, in the bath until it had acquired the proper temperature. The ester was kept in a weighing bottle which contained a little pipette; in this way it was possible to weigh out the ester directly into the solution of barium hydroxide. Errors in volume introduced by this method were found to be negligible. The greatest difficulty, however, lay in finding a means of analysis by which to follow the course of the reaction. Finally, a simple method was adopted. A measured amount of solution was run, by means of a calibrated pipette, into an Erlenmeyer flask and titrated with N/10 hydrochloric acid. Alizarin sulphonate was used as indicator since no sharp "end point" could be determined with methyl orange. Even with this delicate indicator considerable difficulty was experienced; this was true especially at the beginning of the reaction where the concentration of the imidoester relative to the amount of barium hydroxide was fairly large, and where a very small error in titration markedly affects the constant. The calculation of the amount of unchanged ester from these titrations is very simple. Experiment showed that the reaction products contained in the solution do not affect the titration. Thus barium hydroxide could be sharply titrated in the presence of benzamide, which might be formed to some extent by the action of baryta on the first reaction product, benzonitrile; it could likewise be titrated in the presence of benzonitrile and of both compounds at the same time. The neutral tint, when it was once obtained, did not change for several hours. Therefore the amount of acid used in titrating the measured amount of solution represents the total base contained in the given volume; subtracting from this the acid required for the known amount of barium hydroxide, we have, as the remainder, the concentration of unchanged ester. In Tables XV.–XIX. these values are placed in line 2, following $(C-x)$.

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[1] A mercury pump was employed.

[2] The titration was carried out in Nessler tubes.

The amount used for each titration is 50 cc., unless otherwise stated under w; the amount of barium hydroxide contained in the volume titrated is given under ba; the time in minutes is given in line 1, and the velocity constant calculated from equation (15) in line 3. The concentration of ester for each benzoate is approximately the same throughout the series of tables; its value appears in the equation as $(C-x)$ and is given in terms of N/10 alkali.

Methyl Imidobenzoate.

Table XVa.

w = 50 cc. ba = 0.59. Mean, 43430 K_v = 102.

t	0	20	60	80	100	120	140	160
$C-x$	6.60	6.27	5.63	5.44	5.18	5.00	4.78	4.54
K_v	....	(111)	(115)	105	105	100	100	101

Table XVb.

ba = 0.58. Mean, 43430 K_v = 100.

t	0	20	40	60	80	100	120	140	160
$C-x$	5.94	5.66	5.32	5.18	4.88	4.69	4.54	4.34	4.19
K_v	....	105	120	99	107	103	97	97	95

Table XVIa.

ba = 1.14. Mean, 43.430 K_v = 193.

t	0	20	41	60	80	100	120	140	160	180
$C-x$	6.56	5.91	5.33	4.93	4.52	4.21	3.84	3.64	3.31	3.03
K_v	....	(227)	(220)	208	202	193	194	182	188	186

Table XVIb.

ba = 1.20. Mean, 43430 K_v = 203.

t	0	42	60.5	80	100	120	140	160
$C-x$	6.37	5.19	4.72	4.40	4.01	3.64	3.27	3.00
K_v	....	(211)	(215)	201	201	202	207	204

Methyl Imidobenzoate.

Table XVIIa.

ba = 3.18. Mean, $43430\ K_v = 511$.

t	0	21	40	60	80	100	120	140	160	180
$C-x$	5.33	4.17	3.33	2.68	2.18	1.66	1.29	1.02	0.80	0.61
K_v	....	....	500	510	497	485	513	512	514	543

Table XVIIb.

ba = 3.11. Mean, $43430\ K_v = 497$.

t	0	20	42	60	80	100	120	140	160	180
$C-x$	5.47	4.37	3.42	2.76	2.10	1.77	1.37	1.13	0.84	0.65
K_v	....	(487)	(489)	495	519	490	501	488	501	514

Table XVIIIa.

ba = 4.66. Mean, $43430\ K_v = 742$.

t	0	11	20	30	42	50	60.5	70	80
$C-x$	6.40	5.31	4.62	3.90	3.09	2.72	2.33	1.96	1.63
K_v	....	736	(707)	(702)	753	743	(725)	734	743

Table XVIIIb.

ba = 4.80. Mean, $43430\ K_v = 741$.

t	0	10	20	30	40	50	61	70	80
$C-x$	6.37	5.41	4.55	3.80	3.25	2.71	2.24	1.92	1.56
K_v	....	(703)	(723)	745	(729)	741	743	743	(764)

Methyl Imidobenzoate.

Table XIXa.

ba = 7.02. Mean, 43430 K_v = 1090.

t	0.0	10	20	30	40	47	55	62.5	70
$C—x$	5.82	4.58	3.52	2.73	2.07	1.84	1.39	1.17	0.89
K_v	....	1040	1090	1100	1120	1070	1130	1110	1110

Table XIXb.

ba = 7.06. Mean, 43430 K_v = 1090.

t	0.0	10	20	30	40	48	55	63	70
$C—x$	6.16	4.79	3.74	2.85	2.22	1.82	1.58	1.26	0.99
K_v	....	1090	1080	1120	1110	1100	1070	1090	1130

From the data found in these tables it can be shown that the velocity of the decomposition of methyl imidobenzoate in alkaline solution is proportional to the concentration of the hydroxyl ion,

$$K_v = K_{OH} \times C_{OH} \text{ and } K_{OH} = \frac{K_v}{C_{OH}},$$

in which K_v is the observed velocity constant and C_{OH} the concentration of the hydroxyl ion in a given series. C_{OH}[1] is determined from the concentration of the barium hydroxide used and its known degree of dissociation as calculated from its conductivities.[2] The values obtained in this way will be found in Table XX. In column 1 the number of the experiment is given, in column 2 will be found the amount of N/10 barium hydroxide used in 500 cc. of solution, in column 3 the corresponding degree of ionization of the barium hydroxide, in column 4 the concentration of the hydroxyl ion for each cubic centimeter of solution; column 5 contains the observed velocities, K_v, and column 6 this value divided by the hydroxyl concentrations.

Table XX.

1 No.	2 $Ba(OH)_2$.	3 $100\ \alpha_v$.	4 $10^5 \times (OH)$.	5 $43430\ K_v$.	6 $0.434 \times K_{OH}$.
XVa	5.90	97.5	115	102	0.887
XVb	5.80	97.5	113	100	0.885
XVIa	11.40	97	221	193	0.873
XVIb	12.00	97	233	203	0.871
XVIIa	31.80	96	610	511	0.837
XVIIb	31.10	96	597	497	0.833
XVIIIa	46.60	95	886	742	0.840
XVIIIb	48.00	95	912	741	(0.812)
XIXa	70.20	93	1306	1090	0.835
XIXb	70.60	93	1313	1090	0.830

$$\text{Mean, } 0.4343\ K_{OH} = 0.854. \quad K_{OH} = \frac{0.854}{0.4343} = 1.97.$$

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[1] Neglecting the OH ions due to the ester itself. This is exceedingly small in comparison with the OH ions from barium hydroxide since the ionization of a weak base is suppressed by the presence of a strong base.

[2] Kohlrausch and Holbein: "Leitvermögen der Electrolyte," p. 167.

The values in Table XX. for K_{OH} indicate that the hypothesis regarding the proportionality between the velocity of decomposition and the hydroxyl concentration is a correct representation of the facts. Below will be found similarly conclusive evidence in the case of the other esters investigated.

2. *Ethyl Imidobenzoate.*

Tables XXI.–XXIII. give the velocity determinations. In these everything corresponds to the work on the methyl ester. All the solutions were made up to 500 cc. and 50 cc. was used for each titration. The symbols used have the same significance as in the case of the methyl ester.

Ethyl Imidobenzoate.

Table XXIa.

ba = 3.59. Mean, 43430 K_v = 205.

t	0	21	40	60	80	100	120	140	160
$C—x$	5.87	5.33	5.30	4.38	4.06	3.66	3.34	3.00	2.70
K_v	....	199	(110)	210	200	205	204	208	211

Table XXIb.

ba = 3.57. Mean, 43430 K_v = 204.

t	0	20	65	85	105	125	145	165
$C—x$	6.89	6.25	5.14	4.64	4.17	3.84	3.47	3.13
K_v	....	212	195	202	208	202	205	207

Table XXIIa.

ba = 5.22. Mean, 43430 K_v = 299.

t	0	25	35	45	65	85	105	125	145	165
$C—x$	5.88	4.90	4.76	4.23	3.81	3.29	2.85	2.49	2.18	1.89
K_v	....	317	(268)	318	290	296	300	300	298	299

Table XXIIb.

ba = 5.35. Mean, 43430 K_v = 310.

t	0	25	40	50	90	110	130	150	175
$C-x$	6.22	6.08	4.64	4.40	3.27	2.85	2.47	2.07	1.78
K_v	....	(40)	318	301	310	311	308	317	311

Table XXIIIa.

ba = 7.01. Mean, 43430 K_v = 401.

t	0	15	30	45	55	65	75	86	100
$C-x$	6.40	5.58	4.82	4.20	3.87	3.54	3.19	2.90	2.57
K_v	....	398	410	407	397	403	403	400	396

Table XXIIIb.

ba = 7.04. Mean, 43430 K_v = 401.

t	0	25	75	85	110	130	150	175	190
$C-x$	6.16	4.90	3.06	2.83	2.25	1.79	1.56	1.11	0.80
K_v	....	395	404	399	397	412	394	(425)	(466)

Table XXIV.

1 No.	2 $Ba(OH)_2$.	3 $100\,\alpha_v$.	4 $10^5 \times (OH)$.	5 $43430\,K_v$.	6 $0.4343 \times K_{OH}$.
XXIa	35.90	96	689	205	0.298
XXIb	35.70	96	685	202	0.298
XXIIa	52.20	95	992	299	0.301
XXIIb	53.50	95	1070	310	0.290
XXIIIa	70.10	93	(1304)	401	0.307
XXIIIb	70.40	93	(1309)	402	0.307

Mean, $0.43430\,K_v = 0.300$. $K_{OH} = \dfrac{0.300}{0.4343} = 0.69$.

It is evident that the agreement between theory and experiment is as good for the ethyl ester as it is for the methyl ester.

3. n-Propyl Imidobenzoate.

Tables XXV.–XXVII. contain the velocity determinations. The solutions in each case were made up to 500 cc. and 50 cc. was used for each titration.

see errata, p. 823

Table XXVa.

ba = 3.05. Mean, 43430 K_v = 152.

t	0	15	30	50	70	90	130	150	170
$C—x$	3.19	3.03	2.84	2.63	2.47	2.39	1.99	1.88	1.77
K_v	....	150	(170)	(168)	160	144	160	153	150

Table XXVb.

ba = 3.07. Mean, 43430 K_v = 171.

t	0	20	40	60	70	80	100	120	140
$C—x$	3.38	3.16	2.86	2.62	2.51	2.46	2.29	2.14	2.03
K_v	....	146	181	184	185	172	169	174	160

Table XXVIa.

ba = 6.15. Mean, 43430 K_v = 255.

t	0	20	40	60	80	100	120	140	160
$C—x$	3.65	3.29	2.90	2.48	2.27	1.91	1.84	1.64	1.38
K_v	....	226	250	270	258	281	240	250	264

Table XXVIb.

ba = 6.43. Mean, 43430 K_v = 291.

t	0	20	40	60	80	100	120	140	160
$C-x$	3.25	2.72	2.38	2.17	1.92	1.70	1.43	1.28	1.08
K_v	....	(387)	(340)	292	286	281	300	290	298

Table XXVIIa.

ba = 4.56. Mean, 43430 K_v = 207.

t	0	20	40	60	80	100	120	141	160
$C-x$	3.35	2.95	2.74	2.50	2.27	2.13	1.89	1.76	1.55
K_v	....	(276)	218	211	210	197	207	200	209

Table XXVIIb.

ba = 4.62. Mean, 43430 K_v = 210.

t	0	20	40	60	80	100	120	140	160
$C-x$	3.28	2.98	2.57	2.47	2.19	1.99	1.80	1.66	1.47
K_v	....	208	222	205	194	217	217	201	218

Table XXVIII.

1 No.	2 $Ba(OH)_2$.	3 $100\,\alpha_v$.	4 $10^5 \times (OH)$.	5 $43430\,K_v$.	6 $0.4343 \times K_{OH}$.
XXVa	30.50	96	591	152	0.255
XXVb	30.70	96	596	171	(0.285)
XXVIa	61.50	94	1156	255	0.220
XXVIb	64.30	94	1208	291	0.241
XXVIIa	45.60	95	866	207	0.239
XXVIIb	46.20	95	878	210	0.239

Mean, $0.4343\ K_{OH} = 0.239$. $K_{OH} = 0.55$.

4. *Isopropyl Imidobenzoate.*

Tables XXIX.–XXXI. contain the velocity determinations. The solutions in each case were made up to 500 cc. and 50 cc. was used for each titration.

Table XXIXa.

ba = 3.09. Mean, 43430 K_v = 67.6.

t	0	20	30	40	60	80	100	120	156
$C—x$	4.96	4.79	4.73	4.67	4.50	4.34	4.28	4.14	3.90
K_v	....	(75.2)	68.4	65.4	70.4	72.4	64.0	65.4	67.5

Table XXIXb.

ba = 3.22. Mean, 43430 K_v = 67.5.

t	0	40	60	80	100	141	162	175	190
$C—x$	4.97	4.55	4.38	4.27	4.11	3.91	3.77	3.71	3.63
K_v[1]	....	....	(82.0)	69.0	73.6	65.1	66.9	64.9	65.4

Table XXXa.

ba = 4.62. Mean, 43430 K_v = 101.

t	0	20	40	60	80	100	120	140	160
$C—x$	4.69	4.48	4.23	4.11	3.93	3.68	3.59	3.39	3.18
K_v	....	100	112	96	96	105	97	101	105

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[1] Calculated from $t = 40$, $1 - x = 4.55$.

Table XXXb.

ba = 4.65. Mean, 43430 K_v = 109.

t	0	21	40	60	80	100	120	140	160
$C—x$	4.82	4.55	4.29	4.14	3.94	3.75	3.59	3.46	3.22
K_v	....	115	(126)	110	109	109	107	103	110

Table XXXIa.

ba = 6.10. Mean, 43430 K_v = 130.

t	0	23	42	60	80	100	120	140	160
$C—x$	4.54	4.15	3.93	3.78	3.50	3.40	3.16	2.99	2.84
K_v	....	(170)	(150)	133	141	126	131	130	127

Table XXXIb.

ba = 6.16. Mean, 43430 K_v = 128.

t	0	23	41	60	80	101	120	140	160
$C—x$	4.26	3.92	3.63	3.58	3.36	3.14	3.01	2.88	2.63
K_v	....	(160)	(170)	130	131	127	126	122	131

Table XXXII.

1 No.	2 Ba(OH)$_2$.	3 100 α_v.	4 $10^5\times(OH)$.	5 $43430\times K_v$.	6 $0.4343\times K_{OH}$.
XXIXa	30.90	96	593	67.6	0.114
XXIXb	32.20	96	618	67.5	0.109
XXXa	46.20	95	878	101	0.115
XXXb	46.50	95	884	109	0.123
XXXIa	61.50	94	1156	130	0.113
XXXIb	61.60	94	1158	128	0.111

Mean, $0.4343\ K_{OH} = 0.114$. $K_{OH} = 0.265$.

5. *Methyl Imido-m-nitrobenzoate.*

Methyl imido-*m*-nitrobenzoate was prepared from its hydrochloride by treating this with three times the required amount of a cold 30 per cent solution of sodium hydroxide and rapidly extracting the base with ether. The extract was dried and the ether evaporated at reduced pressure, leaving the ester behind as a yellow solid. Upon crystallization from low boiling ligroin, this was obtained as a white, crystalline substance melting at 53°. Dissolved in hydrochloric acid and heated, it yielded *m*-nitrobenzoic methyl ester, melting at 70°. On account of the slight solubility of the ester in water, one liter of a N/200 solution was made up for each velocity determination, and 100 cc. were used for each titration. It was impossible to titrate these solutions in the ordinary way; the lack of a sharp change of tint, even with the help of alizarin sulphonate, made it necessary to titrate in Nessler tubes, using as a standard tint for the end point of the reaction a faintly alkaline solution of alizarin sulphonate. Even under these conditions considerable difficulty was experienced in making the titrations at the beginning of the reaction. The indistinct color change, mentioned above,[1] is not the only difficulty. In the case of the nitrobenzoate a brownish compound seems to be formed as a result of an action of the ester on the indicator. The formation of this substance produces a color change similar to that produced by making the acid solution alkaline, and only by very rapid titration could the confusion resulting from this secondary reaction be avoided. Below are given the results of the velocity reactions; the symbols have the same significance as in the previous experiments.

[1] Page 745.

see errata, p. 823

Table XXXIII.

ba = 3.27. Mean, 43430 K_v = 510.

t	0	19	33	59	70	83	100	115
$C—x$	2.57	2.08	1.86	1.31	1.17	1.01	0.79	0.64
K_v	....	500	(440)	500	500	500	520	530

Table XXXIV.

ba = 4.37. Mean, 43430 K_v = 690.

t	0	12	22	34	42	55	66	80	88
$C—x$	2.32	1.92	1.68	1.35	1.15	0.89	0.78	0.65	0.46
K_v	....	680	640	690	700	(750)	720	690	(790)

Table XXXV.

ba = 6.25. Mean, 43430 K_v = 930.

t	0	20	34	65	75	88	100	110
$C—x$	3.50	2.23	1.55	0.91	0.73	0.57	0.35	0.25
K_v	....							

Table XXXVI.

1	2	3	4	5	6
No.	$Ba(OH)_2$.[1]	100 α.	$10^5 \times (OH)$.	43430 K_v.	0.4343 K_{OH}.
XXXIII	32.70	96	314	510	1.62
XXXIV	43.70	95	415	690	1.66
XXXV	62.50	96	600	930	1.55

Mean, 0.4343 K_{OH} = 1.61. K_{OH} = 3.7.

PART III.

The Velocity of Decomposition of Imidoesters in Aqueous Solution.

Besides the study of the velocity of decomposition of imidoesters under the influence of added acids or alkalis, an investigation of the velocity of decomposition of methyl imidobenzoate in aqueous solution was undertaken, since only a few preliminary determinations had been carried out by Derby.[2] The experimental results are given below; they agree perfectly with the preliminary determinations just mentioned. The theoretical interpretations which should be placed on these results is a question of peculiar interest. Qualitatively, the chief reaction[3] in aqueous solution has been found to be the same as in alkaline solutions—a nitrile and an alcohol are formed. Quantitatively, the velocity determinations of the decomposition gave a constant according to the simple logarithmic function,

$$k_{ester} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (27).$$

This is the equation for a monomolecular reaction which proceeds proportionately to the concentration of the total substance.

In an aqueous solution of a substance like methyl imidobenzoate, which is a very weak base and also, as shown in Part II., a still weaker acid, we must have both its positive and its negative ions. Since these ions will be present only in very small amounts, practically all of the imidoester must be

[1] Column 2 represents in this table the cc. N/10 $Ba(OH)_2$ in 1 liter of the mixture.

[2] THIS JOURNAL, **39**, 471.

[3] It is likely that an acid amide is to a small extent formed in a parallel reaction.

in the nonionized form. Calculations made with the aid of the affinity constant for the base as determined by Derby[1] show that in one-twentieth molar solution about 0.03 per cent of the free base is ionized and in one-hundredth molar solution less than 0.1 per cent is ionized. It is clear, therefore, that the concentration of the nonionized molecule may be put equal to the concentration of the total substance; and that consequently the constant obtained by the logarithmic function (27) would be the true constant giving the velocity of the reaction if the nonionized molecule forms the chief reacting substance in these solutions and breaks down into a nitrile and alcohol according to the equation

$$C_6H_5C(:NH)OCH_3 = C_6H_5C \vdots N + HOCH_3 \qquad (28).$$

It should be noted that although the products in this reaction are also ultimately a nitrile and an alcohol, as in strongly alkaline solutions, the reaction equations in the two cases are different. In the latter instance, we have the reaction expressed by equation (26),[2] which shows that the negative ions are breaking down into nitriles and alcohol ions ($\overset{-}{OR}$). As was to be expected, the characteristic velocity constants for the two different reactions are different. K_{OH}, the velocity constant for the decomposition of the negative ion when one gram molecule of ester is acted upon by one gram ion of hydroxyl was found to be 1.97 for methyl imidobenzoate, and K_{ester}, the constant calculated from (27), according to which the nonionized molecule breaks down, is only 0.00028. So even if both the negative ions and the nonionized imidoesters should give qualitatively the same ultimate products, it is obvious that the negative ions are by far the more reactive constituents in the solution; and, therefore, the rate of change of the nonionized molecules would become of moment only when, by an enormous advantage in concentration, their decomposition becomes the fundamental one. This view, of course, is the simplest possible one based on the fact that the velocity of the decomposition of the methyl imidobenzoate in aqueous solution is found to be determined by the logarithmic equation (27).

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[1] *Loc. cit.*

[2] P. 742.

Before accepting this view, however, of the decomposition of the nonionized molecule, we shall also consider the fact that both the positive and the negative ions which must be present in the solution must also be decomposing as established in Parts I. and II., and we shall try to determine whether, small as their concentrations are, their relatively very great rates of decomposition cannot account for the actual velocity of decomposition observed in aqueous solution.

Since the decomposition constant for the negative ion is very much larger than for the positive imidoester ion, and since the aqueous solution of the free base is strongly alkaline, we might very well have a case of auto-catalysis in which the reaction proceeds exactly as in the presence of hydroxyl ions from barium hydroxide. On this account we shall first consider whether the observed velocity of decomposition can be accounted for as due simply to the decomposition of the imidoester under the influence of the hydroxyl ions produced from itself. The fundamental equation which would apply to such a reaction is

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times C_{OH} \tag{13}$$

Whereas in the presence of barium hydroxide C_{OH} is a constant throughout the course of the experiment and variable only by way of different original concentrations of the hydroxide, in the case under discussion C_{OH} is a variable depending on the concentration of the reacting ester itself. There are two possibilities to be considered in endeavoring to establish the nature of this dependence. First, the concentration of the hydroxyl ion at any moment could be taken as dependent essentially on the ionization of the imidoester as a base alone, on the assumption that the acid character of the imidoester is so exceedingly weak that formation of more positive ions from a salt —which in turn would effect the concentration of the hydroxyl ion—would be so slight as to be negligible in the application of the general equation

$$\frac{C_{pos.\ ion} \times C_{OH}}{C_{mol.}} = K_{aff.} \qquad (29).$$

On this assumption we would obtain a *maximum* concentration of the hydroxyl ions to be used in connection with equation (13), and this is quite sufficient for our purpose. On the basis of such an assumption,

$$C_{OH} = \sqrt{K_{aff.} \times C_{mol.}},$$

and putting $C_{mol.} = C_{ester}$ we have

$$C_{OH} = \sqrt{K_{aff.} \times C_{ester}} \qquad (30).$$

Combining (30) and (13), we find

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times \sqrt{K_{aff.} \times C_{ester}}\ ,$$

$$= K_{OH} \times (C-x) \times \sqrt{K_{aff.} \times (C-x)} \qquad (31).$$

This, on integration, becomes

$$K_{OH} = \frac{2}{t_2 - t_1} \sqrt{\frac{1}{K_{aff.}}} \left\{ \frac{1}{(C-x_2)^{1/2}} - \frac{1}{(C-x_1)^{1/2}} \right\} \qquad (32).$$

The values for K_{OH}, calculated according to this equation (32), gave, indeed, a tolerably good constant for the whole course of each individual experiment carried on through a period of from seventy to eighty hours for each concentration; they did not, however, give the same constant for the varying original dilutions of the ester; and the constants were all *very much larger than the same constant*, K_{OH}, determined for the same ester by the action of barium hydroxide, as given in Part II.

In the following table, the first line, after V, gives the volume in liters containing a gram molecule of the free imidoester; the second line, after $K_{mol.}$, gives the constant calculated according to equation (27), referring the active mass of the changing substance to the nonionized molecule, and the third line, after K_{OH}, gives the average constants calculated according to (32), on the assumption that the reaction in aqueous solution is a case of auto-catalysis, the hydroxyl ion of the free base catalyzing the ester in the same way as barium hydroxide does.

Table XXXVII.

V	21.7	47.0	83.3	125
$K_{mol.}$	0.00028	0.00026	0.00026	0.00024
K_{OH}	22.6	30.1	40.7	45.2

The constant K_{OH} obtained in alkaline solutions by the addition of varying amounts of barium hydroxide to the aqueous solution of the free base is 1.97 (see p. 749, Table XX.). Since K_{OH}, as determined for the pure aqueous solution, is very much larger[1] than 1.97 and is not a constant for different dilutions, we are led to the conclusion that the reaction is not a case of auto-catalysis and that the chief reacting substance must be the nonionized molecule of the free base, breaking down, very slowly but with a constant velocity, in the course of seventy hours, into nitrile and alcohol. The important point in this conclusion is the fact that, having established in Parts I. and II. that both the positive and the negative ions of the imidoesters show characteristic, specific reactions proceeding with constant velocities, we now find that the third form of the esters, the nonionized form, also is active, changing exceedingly slowly, compared with the other forms, but with a measurable velocity[2] according to the equation

$$C_6H_5(:NH)OR = C_6H_5C\vdots N + HOR \qquad (33).$$

In this calculation of C_{OH}, it will be recalled, the salt formation between the acid and the basic parts of the amphoteric was considered negligible (in equation 29). This was done because the basic functions are far more pronounced than the acid functions, as is shown by the marked alkaline reaction of the ester's aqueous solution. Taking the amphoteric character of imidoesters into account, we would have the case of salt formation between a weak base and a very weak acid. Consequent hydrolysis of the salt would establish the condition of equilibrium expressed by the formulation

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[1] The calculation was made on the assumption of a *maximum* possible concentration of OH ions (equation 29, p. 764), and K_{OH} would be still larger if the concentration of the OH ion were smaller, consequently the conclusions drawn in the text hold independently of this assumption.

[2] The importance of this question of the decomposition of the nonionized molecule is such that Mr. B. B. Freud will continue this part of the investigation to develop a broader range of experiments.—J. STIEGLITZ.

$$\underset{\text{base}}{C_6H_5C(NH)OCH_3} + \underset{\text{acid}}{C_6H_5C(:NH)OCH_3} \rightleftarrows [C_6H_5C(:NH)OCH_3]_2 \qquad (33).$$

Salt and acid formation take place, of course, at the imide (:NH) group in the molecule. In such solutions, we would have for the very weak acid:

$$\frac{C_H \times C_{neg.\,ion}}{C_{ester}} = k_{acid} \qquad (34),^{1}$$

and for the weak base

$$\frac{C_{OH} \times C_{pos.\,ion}}{C_{ester}} = k_{base} \qquad (35).^{1}$$

Combining (34) and (35), we have, as usual, for the hydrolysis of salts of weak acids and weak bases,

$$\frac{C_{neg.\,ion} \times C_{pos.\,ion}}{C^2_{ester}} = \frac{k_{acid} \times k_{base}}{k_{H_2O}} = k \qquad (36).$$

If the positive and negative ions are formed chiefly from the salt, as in the case of aniline acetate,[1] we may consider

$$C_{neg.\,ions} = C_{pos.\,ions},$$

and we would have

$$\frac{C^2_{neg.\,ion}}{C^2_{ester}} = K \qquad (37),$$

$$C_{neg.\,ions} = k'C_{ester} \qquad (37').$$

In a word, if salt formation does occur in the case of such an amphoteric substance, which is a weak base and a weak acid, to an extent such as to make the salt, rather than the base or acid, the chief source of the ions of the organic compound, then the concentration of the negative ions would be in practically constant proportion to the concentration of the total ester. Therefore, a reaction proceeding at a rate proportionate to the total ester would proceed also proportionately to the concentration of the negative ion. The reaction might also, on this account, be a function of the concentration of the negative ion, considered as the "active mass." This possibility is actually realized in the experimental results for the decomposition of methyl imidobenzoate in water solution —the rate of change is actually proportional to the total ester. This result in itself has justified us, in the study of the theory of the case, in not being content with only the first conclusion, *viz.*, that the nonionized imidoester *must* constitute the decomposing "active mass."

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[1] The concentration of the nonionized molecule may be put equal to that of the ester.

[2] Arrhenius: Z. physik. Chem., **5**, 19 (1890).

It will be recalled also that the fundamental equation,

$$\frac{dx}{dt} = K_{OH} \times C_{ester} \times C_{OH} \qquad (13),$$

is the experimental equation, identical with the one based on the theory of catalysis in alkaline solution, according to which negative ions represent the decomposing substance. This latter equation was written

$$\frac{dx}{dt} = K_{ion} \times C_{neg.\ ion} \qquad (23).$$

Theoretically, therefore, a reaction proceeding with a velocity directly proportional to the concentration of the total ester could be satisfied also by a constant representing the rate of change as proportional to the concentration of the negative ion of the *amphoteric* substance (equation 37′). The only question to be answered for the substance under investigation is whether the actual rate of change, as experimentally determined, agrees in value with that deduced from theory. This test may be made as follows:

Above it was shown that on the basis of an assumption that C_{OH} has a maximum value, the decomposition in aqueous solution is far too rapid to be considered a case of auto-catalysis. On the present assumption that the concentration of the positive ester ion is perceptibly increased by salt formation, C_{OH} (equation 29) and consequently also $C_{neg.\ ion}$ (equation 22)[1] must have still smaller values: the reaction ought to proceed more slowly and this would be in still greater discrepancy with the experimental fact.

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[1] This was established in Part II. and the whole argument rests on that work.

We are obliged to conclude again, therefore, that in aqueous solution methyl imidobenzoate decomposes into nitrile and alcohol with a speed too great to be accounted for on the assumption that it is proportional to the concentration only of the negative ion, as was found to be the case in strongly alkaline solutions.

The decomposition, which occurs simultaneously with that of the negative ion, of the positive ion into ammonia and ester (Part I.) is far too slow, in the minimal concentrations in which it is present, to account for this excessive speed. The velocity constant for that change is 0.0063 for methyl imidobenzoate (see Part I., p. 737, Table XIV., column 4). For a twentieth molar solution, the original concentration of the positive ion calculated from the affinity constant,

$$C^2_{ions} = 0.5 \times 10^{-8} \times C_{mol.},$$

is

$$C_{ion} = 0.000015.$$

The original rate of change of the ion referred to a whole gram molecule of the ester would be

$$0.000015 \times 0.006 \times 20 = 0.0000018,$$

a quantity which is negligible in accounting for the observed rate of change of one gram molecule total substance, *viz.*, 0.00028.[1]

EXPERIMENTAL.

The analytical method of following the decomposition of methyl imidobenzoate in aqueous solution was practically the one employed for the study of the decomposition of the same substance in strongly alkaline solution (see p. 745). Since the reaction proceeded very slowly, titrations were made at long intervals and special care was taken that no variations should occur in the temperature, the bath being kept at 25° (±0°.01) for several days. The logarithmic equation

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[1] Only traces of ammonia and ester are formed, as a matter of fact.

(27) was used for obtaining the constants, $K_{mol.}$, given in the third columns of the following table, and equation (32) was used for the determinations of the values of K_{OH} (the fourth column). For these calculations, equation (32) is best transformed as follows: Calling the original concentration of the base 1 gram molecule in V liters and x_t the part of a gram molecule changed in t minutes, we have:

$$C = \frac{1}{V} \text{ and } C - x = \frac{1 - x^t}{V}.$$

If v_0 cc. and v_t cc. acid were used to neutralize the free base present in a measured amount of solution when $t = 0$ and $t = t$ (*e. g.*, 4.62 cc. and 4.34 cc., in Table XXXVIII., when $t = 0$ and $t = 288$), then the unconsumed part, $(1 - x_t)$, of the free base may be expressed by

$$1 - x_t = \frac{v_t}{v_0}.$$

Equation (32) acquires the very simple form:

$$K_{OH} = \frac{2}{t}\sqrt{\frac{V}{K_{aff.}}}\left\{\sqrt{\frac{v_0}{v_t}} - 1\right\} \qquad (32').$$

Column 1, in the following tables, gives the time in minutes; column 2, the number of cc. 0.1 normal acid required to neutralize w cc. of the solution.

Table XXXVIII.

$V = 21.7$. $w = 10$ cc.

t.	v_t.	$43430 K_{mol.}$	K_{OH}.	t.	v_t.	$43430 K_{mol.}$	K_{OH}.
0	4.62	....	....	1963	2.60	12.7	22.6
288	4.34	(9.0)	(14.6)	2948	2.01	12.7	23.2
338	4.18	12.8	20.3	3169	1.80	12.9	25.2
438	4.13	11.1	17.5	3360	1.76	12.4	24.6
1521	3.00	12.3	21.0	4290	1.44	11.8	24.5
1684	2.88	12.2	20.9	4635	1.33	11.8	23.7

Mean, $K_{mol.} = 0.00028$. Mean, $K_{OH} = 22.4$.

Table XXXIX.

$V = 47$. $w = 10$ cc.

t.	v_t.	43430 $K_{mol.}$	K_{OH}.	t.	v_t.	43430 $K_{mol.}$	K_{OH}.
0	2.13	....	....	1935	1.24	12.0	31.1
266	1.92	(17.0)	(37.4)	2826	1.08	10.4	25.8
414	1.87	(13.6)	31.7	3143	0.99	10.6	29.5
1498	1.46	11.0	27.1	3338	0.90	11.2	31.5
1660	1.39	11.1	28.0	4265	0.69	11.4	34.7
1765	1.36	11.0	27.9	4553	0.67	11.0	33.7

Mean, $K_{mol.} = 0.00026$. Mean, $K_{OH} = 30.1$.

Table XL.

$V = 83.3$. $w = 25$ cc.

t.	v_t.	43430 $K_{mol.}$	K_{OH}.	t.	v_t.	43430 $K_{mol.}$	K_{OH}.
0	3.00	....	....	1926	1.80	11.5	39.3
122	2.90	12.0	36.0	2817	1.42	11.1	41.9
295	2.84	(9.0)	42.2	3191	1.34	10.1	40.4
464	2.54	(15.5)	48.7	3327	1.24	11.2	43.4
1489	2.00	12.0	39.3	4260	1.00	11.2	44.7
1651	1.94	11.4	36.3	4614	0.95	10.8	43.6

Mean, $K_{mol.} = 0.00026$. Mean, $K_{OH} = 40.7$.

Table XLI.

$V = 125$. $w = 50$ cc.

t.	v_t.	43430 $K_{mol.}$	K_{OH}.	t.	v_t.	43430 $K_{mol.}$	K_{OH}.
0	4.00	....	....	1780	2.57	10.8	44.7
202	3.77	11.0	47.6	2793	2.09	10.1	44.0
437	3.67	(8.5)	(32.25)	3165	1.91	10.1	44.9
1460	2.90	9.0	38.3	3301	1.85	10.1	45.6
1653	2.67	10.1	43.4	4233	1.49	10.1	48.3
				4586	1.35	10.2	50.4

Mean, $K_{mol.} = 0.00024$. Mean, $K_{OH} = 45.2$.

It will be seen that $K_{mol.}$ does not vary with V, its average being 0.00026.[1] The relation existing between V and K_{OH} as well as between this K_{OH} and the K_{OH} determined from the velocity in strongly alkaline solutions, has been fully discussed.

The experimental data of this investigation have justified us in certain definite conclusions, which shall be briefly stated here:

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[1] Derby found 0.00028.

I. The speed of the decomposition of the imidoester salts by water is dependent on their positive ions as is shown in Part I. The velocity is proportional to the concentration of the ions, but is also influenced by a "salt effect," which is due to the imidoester salt itself. We have here, in other words, an "auto-salt effect." The reaction is represented by the equation

$$RC(:\overset{+}{N}H_2)OR' + H_2O = RCOOR' + \overset{+}{N}H_4.$$

II. The imidoesters are amphoteric in character; the negative ions decompose into nitriles and alcohol (ions) with a velocity proportional to their concentration. Since the acid ionization is very slight, the concentration of negative ions is proportional to that of the ester and that of the hydroxyl ions, and therefore the action has the appearance of a so-called "catalytic" action of hydroxyl on the molecular ester. The reaction is represented by the equation

$$RC(:\overline{N})OR' = RCN + \overline{O}R'.$$

III. The nonionized molecules appear to decompose also into nitriles and alcohols with a much smaller velocity than that exhibited by the negative ions. The reaction is given by the equation

$$RC(:NH)OR' = RCN + HOR.$$

In conclusion, the writer takes pleasure in acknowledging gratefully his appreciation of Dr. Stieglitz's suggestive guidance of his work, and of the interest he has taken in it.

THE DECOMPOSITION OF CERTAIN MINERALS AND INDUSTRIAL PRODUCTS BY MEANS OF SODIUM PEROXIDE AND METALLIC SULPHIDES.

By James H. Walton, Jr., and Herman A. Scholz.

In the year 1893 J. Clark[1] published a method for decomposing pyrites, zinc blende, galena, chromium, and arsenic ores by mixing them with sodium peroxide in an open platinum or nickel dish and fusing in the usual manner. W. Hempel[1] used a similar method for the decomposition of chromium, manganese, tungsten, and titanium ores. Spüller and Kalman,[2] Edinger,[3] Saniter,[4] Glaser,[5] Angenot,[6] and Lucchese[7] used sodium peroxide for the decomposition of various organic and inorganic substances. These investigators all followed the method of placing the substance to be decomposed in a crucible, mixing with sodium peroxide, and applying heat to the crucible. While the decompositions made in this way are very complete, the sodium peroxide attacks the crucible vigorously, and a large amount of foreign matter is consequently introduced into the determination.

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[1] J. Chem. Soc., **53**, 1079–1083 (1893).

A number of investigators have published methods of decomposition in which the heat necessary to bring about the decomposition is furnished by the reaction between the peroxide and some organic substance present in the mixture. S. W. Parr[8] decomposed coal by mixing it in a steel bomb with sodium peroxide and igniting the mixture by dropping a red-hot iron wire into the mass, the combustion taking place without further application of heat. Although this method was used primarily for the determination of the heating power of coals, it was found that the sulphur was completely oxidized to the sulphate and could be determined in the usual manner.

Pringsheim[9] used a similar method for the quantitative and qualitative determination of the halogens, arsenic, and phosphorus in organic compounds. Von Konek[10] also used this method for making qualitative analyses of organic substances, using a cylindrical nickel or steel crucible similar to that designed by Parr for use in his calorimeter. The finely powdered sample, in this case, was mixed with sodium peroxide and a compound rich in carbon, such as camphor, and the mass ignited by dropping in a red-hot iron wire.

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[1] Z. anorg. Chem., **3**, 193–194 (1893).

[2] Chem. Ztg., **17**, 881, 1207, 1360, 1412 (1892); **18**, 292 (1893).

[3] Z. anal. Chem., **34**, 362–368 (1895).

[4] Chem. Ztg., **19**, 1657 (1898).

[5] J. Am. Chem. Soc., **20**, 130–133 (1898).

[6] Z. ang. Chem., **17**, 1274 (1904).

[7] Ann. chim. anal. appl., **9**, 450 (1905).

[8] J. Am. Chem. Soc., **22**, 646 (1900).

[9] THIS JOURNAL, **31**, 386 (1903); Ber. d. chem. Ges., **37**, 2155 (1904); **38**, 2436 (1906).

[10] Z. ang. Chem., **17**, 771, 1093 (1904).

The decomposition of substances by means of the heat obtained from the action of the sodium peroxide on an organic compound mixed with the substance has several advantages. In the first place, the vessel in which the decomposition is carried out is attacked to an extent which is for many purposes inappreciable. Moreover, the decomposition is completed in a very few minutes. It seemed to the authors that this method could be modified and used to decompose certain substances of technical importance, particularly those which require the use of nitric acid for their decomposition, the excess of which must often be removed by evaporation with sulphuric acid before the determination can be made.

EXPERIMENTAL.

The sodium peroxide used in these experiments was the ordinary commercial article manufactured by Koenig & Co. It contained traces of SiO_2, Al_2O_3, and Fe_2O_3. Its purity was determined by measuring the volume of oxygen which was given off from a weighed amount of the substance when decomposed by water containing a few drops of a dilute solution of cobalt nitrate.[1]

The sample used in this work contained between 95 and 96 per cent sodium peroxide.

The Decomposition of Substances containing Lead.

a. Galena Ores.—Two galena ores were used in testing this method of decomposition. The percentage of lead present was first determined gravimetrically by boiling the finely ground ore (passed through a 200-mesh sieve) with concentrated nitric acid and a small amount of hydrochloric acid for one and a half hours, precipitating the lead as the sulphate, filtering, separating the lead sulphate from the residue by dissolving in hot ammonium acetate solution, reprecipitating by means of sulphuric acid, and weighing the lead sulphate on a Gooch crucible.

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[1] Archbutt: Analyst, **20**, 3 (1895).

The following values were obtained:

	Per cent of lead.	
	1.	2.
Ore No. 5	61.58	61.52
Ore No. 22	56.05	55.98

These iron ores contained a small amount of iron pyrites and a little silica. Long boiling with acid was found to be absolutely necessary to completely decompose them. In one case in which the ore was boiled for only one-half hour, results were obtained which were several per cent lower than those given above. The above results were taken as the true values for these ores as they agree with analyses made later by different methods.

For the purpose of determining the right kind of sodium peroxide mixture to decompose these ores, a number of qualitative experiments were made in which the ores were placed in the bomb of a Parr calorimeter and mixed with sodium peroxide and various easily oxidizable substances such as magnesium, ammonium oxalate, and starch. The thoroughly mixed charge was ignited by dropping a red-hot piece of iron wire into the water-cooled bomb. When starch was used the mass fused quietly. It was found that the addition of a small amount of potassium persulphate to the sodium peroxide gave a better fusion and an apparently complete decomposition of the ore.[1]

The following quantitative experiment was carried out:

Experiment 1.

0.3 gram ore No. 5 (200-mesh sieve).
5.0 grams sodium peroxide.
0.2 gram starch.
0.3 gram potassium persulphate.

This mixture was ignited in a closed bomb by means of a fine iron wire which passed through the charge, and which was heated to a red heat by means of an electric current.

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[1] S. W. Parr: J. Am. Chem. Soc., **24**, 167 (1902).

The melt was dissolved in 100 cc. of water and enough sulphuric acid added to neutralize the alkali and leave an excess of 2 per cent acid. Sodium bisulphite was added to reduce the lead peroxide and the solution was boiled for five minutes. It was then diluted and the lead determined gravimetrically as the sulphate.

The following results were obtained:

	Per cent of lead.		
Ore No. 5	57.49	60.22	59.13

In these experiments it was observed that the fusion did not take place quietly, but was attended by slight explosions, which threw the fused mass upon the side of the bomb. It seemed reasonable to believe that this fact might be the cause of the low results.

Zinc sulphide, when mixed with sodium peroxide and ignited, is oxidized with the evolution of great heat, the oxidation taking place quietly, however. The following quantitative experiment was made in which this substance was substituted for the starch. The zinc sulphide used was the dry, finely divided product prepared by Kahlbaum.

Experiment 2.

0.5 gram ore.
8.0 grams sodium peroxide.
0.8 gram zinc sulphide.
0.3 gram potassium persulphate.

The mixture was placed in an open bomb and ignited as before. The entire mass became liquid and red-hot, and the fusion took place without any spattering. The following results were obtained:

	Per cent of lead.	
	1.	2.
Ore No. 5	60.61	59.73
Ore No. 22	55.51	55.18

In this series the lead sulphate was determined by titrating the ammonium acetate solution of lead sulphate with ammonium molybdate according to Alexander's method,[1] the melted mass from the fusion being treated in other respects as in Experiment 1. The results obtained in the analysis of the two ores are somewhat better than those obtained when starch was used, but they are from 0.5 to 1.00 per cent lower than the values obtained by the acid decomposition method.

In several cases in which the above charge was used the decomposition was found to be incomplete, a slight amount of the ore remaining undecomposed in the sharp edge of the bomb at the point at which the wall and bottom intersect. It was apparent that this part of the bomb did not become sufficiently hot to decompose the ore. Since the fusion takes place quietly, it was found possible to avoid this uncertainty of decomposition by using a nickel crucible which has rounded edges and consequently affords no place for the ore to lodge. Moreover, the melt could be more easily removed and less water was needed for its solution. The nickel crucible used had a capacity of 30 cc. and was 1 $^5/_8$ inches in diameter. The charge was placed into the crucible and ignited by means of a short piece of magnesium ribbon instead of iron wire, which caused considerable trouble by forming the magnetic oxide of iron. This compound, being difficultly soluble, remains as a residue and makes it very difficult to tell whether or not the ore is completely decomposed.

Experiment 3.—The charge used was the same as in Experiment 2. The dry, finely ground sodium peroxide was measured by means of a small aluminum scoop. The other substances were added and thoroughly mixed by means of a glass rod, which was then brushed clean. The cover was placed upon the crucible and was moved far enough to one side to permit the dropping in of a piece of lighted magnesium ribbon about one-half inch in length.

After the ignition had taken place the crucible was immediately covered. The lead was determined by the molybdate method, the following results being obtained:

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[1] Alexander: Eng. and Min. J., **13**, 55. See also Bull. School of Mines Quarterly **23**, 348 (1902).

	Per cent of lead.	
	1.	2.
Ore No. 5	61.23	61.22
Ore No. 5 (gravimetrically)	60.68	59.07
Ore No. 22	55.82	55.68

These low results might be due to incomplete decomposition, although, from the fact that no residue could be seen on dissolving the fusion in acid, this seemed improbable. To test this point, however, a sample of the ore was fused with sodium peroxide in an iron crucible, the heat being supplied by a Bunsen burner.

Experiment 4.

0.3 gram ore No. 5
5.0 grams sodium peroxide.

This mass was kept in a molten condition for five minutes and the lead determined gravimetrically. The results were low, 60.07 and 60.06 per cent of lead being found in duplicate determinations.

It will be seen that the results obtained with ore No. 5, in Experiments 2, 3, and 4, vary between 59.07 and 61.23. It was noticed that in the experiments in which the lowest results were obtained the precipitate of lead sulphate was colored dark brown, due to basic sulphates of iron which are precipitated upon boiling in a slightly acid solution when large quantities of alkali salts are present.[1] It occurred to the authors that these basic iron salts kept the lead sulphate from being dissolved by the ammonium acetate solution, the effect being similar to that produced by the presence of barium sulphate.[2]

To test this idea the following experiments were carried out:

Experiment 5.—A fusion of ore No. 5 was made as in Experiment 3 and the melt treated as before, except that the boiling on acidifying was omitted in order to prevent, as much as possible, the formation of the basic iron salts. The solution was heated to the boiling point and then allowed to cool. The residue still had a brown color, but it was much lighter than before. The lead was determined by the molybdate method, the percentages found being 61.23 and 61.16.

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[1] Pickering: J. Chem. Soc., **37**, 807 (1880).

[2] Bull. School of Mines Quarterly, **23**, 348 (1902).

Experiment 6.—This fusion was also carried out as in Experiment 3. The crucible and melt were put into a casserole and about 75 cc. of water containing 7 cc. of sulphuric acid (sp. gr. 1.84) were added. Enough sulphuric acid was present to neutralize all of the alkali. The melt dissolved in two of three minutes and the crucible was immediately removed. An excess of 4 cc. of sulphuric acid (sp. gr. 1.40) was then added, and a concentrated solution of sodium bisulphite poured in to reduce the lead peroxide. The solution was boiled for a minute, diluted to 200 cc., cooled, and 20 cc. of 95 per cent alcohol added. The residue was almost pure white. The lead was determined by the molybdate method, 61.46 per cent being found present. On repeating the determination, following the procedure described, the values 61.51 and 61.57 per cent were obtained.

Ore No. 22 was analyzed by the same method, 55.89 and 55.88 per cent of lead being obtained. These results agree closely with those obtained by the acid decomposition method. It seems logical to conclude that the low results were due to the presence of the basic salts of iron. The formation of these basic salts may be avoided by dissolving the fusion in acidified water.

In order to determine the value of the above method of decomposition as a general method for the decomposition of other substances containing lead, experiments were carried out in which some typical substances were analyzed by the sodium peroxide method, and also by the standard method.

Experiment 7.—A low grade galena ore (No. 45), high in both silica and iron pyrites, was decomposed by boiling with nitric and hydrochloric acids, and the lead determined gravimetrically, 3.13 per cent lead being found. The ore was also decomposed by means of the following charge:

1.00 gram ore No. 45 (through 200-mesh sieve).
10 grams sodium peroxide.
0.8 gram zinc sulphide.
0.3 gram potassium persulphate.

The mixture was ignited by means of a magnesium ribbon. A very hot fusion was obtained, due to the oxidation of the pyrite in the sample. The melt was treated as in Experiment 6 and the lead determined by titration with ammonium molybdate solution, the values 3.16 and 3.19 per cent of lead being obtained in duplicate determinations.

b. Lead Glaze.—A lead glaze high in calcium and silica was analyzed by the two methods. A one gram sample of the glaze (200-mesh sieve) was decomposed by the nitric acid method and the lead determined by the molybdate method. The large amount of silica caused difficulties both in filtering the insoluble residue and in dissolving the lead sulphate in ammonium acetate solution, necessitating a much longer boiling.

	1.	2.
Per cent of lead in glaze	27.81	27.82

Experiment 8.

1.0 gram glaze (200-mesh sieve).
10.0 grams sodium peroxide.
1.5 grams zinc sulphide.
0.4 gram potassium persulphate.

Since there was no combustible matter in the sample, it was necessary to raise the proportion of zinc sulphide. The fusion was good and the glaze completely decomposed. The melt dissolved in water, the absence of iron making unnecessary the precautions taken in the previous analyses to avoid the precipitation of basic salts. The lead determined by the molybdate method gave 27.84 and 27.82 per cent lead. In this fusion the silica went into solution almost completely and was filtered off from the insoluble residue and thus did not interfere in the filtering nor in the solution of the lead sulphate.

c. Lead Slag.—A sample of 0.5 gram of lead slag (100-mesh sieve) was decomposed by nitric and hydrochloric acids and the lead determined by the molybdate method, 36.39 per cent being found.

Experiment 9.

0.5 gram lead slag (100-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited with magnesium wire. The fusion was good and the decomposition appeared to be complete. Since there was very little iron present, the melt was dissolved in water and treated in the usual manner and the lead determined by the molybdate method. Results were 36.58 and 36.48 per cent lead.

These results by the sodium peroxide method compare very favorably with those obtained by the standard nitric and hydrochloric acid decompositions, as may be better seen from Table I.

Table I.—Comparison of Lead Determinations by Standard and by Sodium Peroxide Methods of Decomposition.

Sample.	Standard method, per cent Pb.	Peroxide method, per cent Pb.
Galena ore No. 5	61.58[1]	61.46
" " " 5	61.62[1]	61.51
" " " 5	...	61.57
" " " 22	56.04[1]	55.89
" " " 22	55.98[1]	55.90
" " " 22	...	55.88
" " " 45	3.13[1]	3.16
" " " 45	...	3.19
Lead glaze	27.81	27.84
" "	27.82	27.88
" slag	36.39	36.48
" "	...	36.58

Sodium Peroxide Method of Decomposition Applied to Manganese Determinations.

Since the sodium peroxide and zinc sulphide mixtures were so effective as fluxes in the lead determinations, they were tried on manganese compound.

a. Analysis of Manganese Glaze.—A manganese glaze high in silica, but containing no calcium, was first used. It was not attacked to any appreciable extent by nitric and hydrochloric acids, even after boiling for an hour. One gram of the glaze (200-mesh sieve) was fused with sodium carbonate in a platinum crucible. The melt was dissolved, made acid with sulphuric acid (sp. gr. 1.42), and the manganese determined by Volhard's[1] method.

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[1] Lead determined gravimetrically as $PbSO_4$.

	1.	2.
Per cent of MnO in the sample:	4.57	4.55

Experiment 10.

1.0 gram manganese glaze (200-mesh sieve).
1.4 grams zinc sulphide.
1.0 gram sodium peroxide.
0.4 gram potassium persulphate.

Ignited in a nickel crucible by means of magnesium ribbon. Very good fusion and apparently complete decomposition, for no residue was left on acidifying with sulphuric acid and adding a little sodium sulphite. The melt was dissolved in water, acidified with sulphuric acid (sp. gr. 1.42), and sodium bisulphite was added to reduce manganese dioxide. The sulphur dioxide was boiled off and the manganese determined by Volhard's method. Results: 4.57 and 4.55 per cent MnO.

b. Analysis of Franklinite.—The sample of franklinite contained considerable silica. As is well known, it is a very refractory mineral which cannot easily be decomposed by sodium carbonate fusion, is decomposed with great difficulty by potassium bisulphate fusion, and is decomposed by concentrated nitric and hydrochloric acids only after long boiling. A one gram sample (200-mesh sieve) was boiled for two hours with nitric acid (sp. gr. 1.42) containing a small quantity of hydrochloric acid (sp. gr. 1.12). Ten cc. sulphuric acid were added and the solution boiled down to sulphuric acid fumes. It was diluted and the manganese determined by Volhard's method. Results were: 7.89 and 7.96 per cent MnO.

Experiment 11.

1.0 gram franklinite (200-mesh sieve).
8.0 gram sodium peroxide.
1.2 grams zinc sulphide.
0.4 gram potassium persulphate.

Ignited by magnesium in a nickel crucible. The mixture became liquid and red-hot but the decomposition was not complete.

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[1] Volhard: Ann. Chem. (Liebig), **198**, 318.

The proportions of the components were varied but it was impossible to get a complete decomposition with these ingredients. It was therefore decided to substitute for the zinc sulphide some substance which would give more heat. Iron pyrites and a small amount of magnesium powder were found to answer this requirement very well.

Experiment 12.

1.0 gram	franklinite (200-mesh sieve).
8.0 grams	sodium peroxide.
0.3 gram	powdered magnesium.
0.3 gram	potassium persulphate.
2.0 grams	pyrite.

Ignited by magnesium wire in a nickel crucible. The fused mass was extremely hot and remained liquid and red-hot for about two minutes. It gave a complete decomposition of the franklinite, but the melt dissolved very slowly, in about two hours. This was remedied by sifting 3 to 4 grams of sodium peroxide into the liquid mass and gently rotating the crucible to mix the peroxide with the molten mass. The contents of the crucible, after cooling, dissolved easily in water in 3 to 4 minutes. The solution was made acid with sulphuric acid (sp. gr. 1.42), the manganese dioxide reduced by sodium bisulphite, and the manganese determined by Volhard's method as in the other determination.

	1.	2.
Percentage of MnO	7.90	7.88

c. Analysis of Ferro-manganese.—A 0.5 gram sample of ferro-manganese which had been passed through a 100-mesh sieve was dissolved by boiling for about an hour in nitric acid (sp. gr. 1.42). Sulphuric acid was added and the solution was evaporated to sulphuric acid fumes. The manganese was determined by Volhard's method as in the franklinite determinations. Results were 56.25 and 56.23 per cent manganese.

Experiment 13.

0.5 gram	ferro-manganese (100-mesh sieve).
8.0 grams	sodium peroxide.
0.8 gram	zinc sulphate.
0.3 gram	potassium persulphate.

Ignited by means of magnesium ribbon. A red-hot liquid mass was obtained, and the substance apparently decomposed completely. The melt dissolved with difficulty. Three to four grams of sodium peroxide sprinkled into the fused mass produced a melt that was dissolved easily in a few minutes. The solution was acidified with sulphuric acid, the manganese dioxide reduced with sodium bisulphite, and the manganese determined by Volhard's method as before. Results: 56.18 and 56.32 per cent manganese.

Table II.—Comparison of Standard and Sodium Peroxide Methods of Decomposition for Manganese Determinations.

Sample.	Standard method, per cent MnO.	Peroxide method, per cent MnO.
Manganese glaze	4.57	4.58
" "	4.55	4.55
Franklinite	7.89	7.90
"	7.96	7.88
	Per cent Mn.	Per cent Mn.
Ferro-manganese	56.25	56.18
"	56.23	56.32

The manganese in each case was determined by Volhard's method.

The Decomposition of Chrome Iron Ore.

For these experiments a chrome iron ore high in chromium was used. It was first analyzed by fusing in a porcelain crucible with sodium peroxide, dissolving the fused mass in water, and destroying the excess of the peroxide by boiling. To the dichromate solution an excess of standard ferrous sulphate solution was added and the excess above that necessary to reduce the sodium dichromate was determined by titrating with standard potassium dichromate. The results obtained were 47.09 and 47.12 per cent Cr_2O_3.

Experiments with a charge similar to that used in Experiment 11 showed that not enough heat is obtained with the zinc sulphide to completely decompose the chrome iron ore.

A mixture of pyrite and magnesium was found to work satisfactorily.

Experiment 14.

0.5 gram chrome iron ore (through 200-mesh sieve).
8.0 grams sodium peroxide.
0.3 gram potassium persulphate.
2.0 grams iron pyrites.
0.3 gram magnesium.

Ignited in the usual manner. The fusion was very hot, but it was necessary to sift 3–4 grams of sodium peroxide in the liquid mass to make it dissolve easily. The chromium was determined volumetrically, 47.07 per cent being found in the sample.

The Application of the Sodium Peroxide Method of Decomposition to Silica Determinations.

In order to investigate the adaptability of the sodium peroxide method to silica determinations, a blast furnace slag was decomposed by this method and by the standard method and the percentages of silica obtained by the two methods compared. For the standard method 1.0 gram of the slag (200-mesh sieve) was boiled for an hour with hydrochloric acid (sp. gr. 1.12). The slag appeared to be completely decomposed. It was evaporated to dryness on the water bath and kept there for several hours after it was dry. It was moistened with hydrochloric acid, dissolved in water, and the silica filtered off. The filtrate was dehydrated a second time. The silica was ignited to constant weight in a platinum crucible and then volatilized in the usual manner, the silica being determined by difference. The results obtained were 30.06 and 30.04 per cent SiO_2.

Experiment 15.

0.5 gram slag (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited the above mixture by means of magnesium ribbon in a nickel crucible. A good fusion was obtained. The melt dissolved easily in water and no residue was left on acidifying with hydrochloric acid. The silica was dehydrated twice and determined as before. The results were 30.02 and 29.98, as against 30.04 and 30.06 per cent by the standard method.

Qualitative Experiments.

Qualitative experiments were carried out in order to test the adaptability of this method to the decomposition of various substances.

a. Monazite.—The sodium peroxide method of fusion was tried on a sample of monazite containing 2.75 per cent ThO_2.

Experiment 16.

1.0 gram monazite (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited the above mixture with magnesium ribbon. The decomposition was complete, for upon acidifying with hydrochloric acid no residue was left.

b. Clays.—A brick clay of the following composition was used: SiO_2, 60.93; Al_2O_3, 17.93; Fe_2O_3, 8.12; MgO, 0.91; CaO, 1.35; Na_2O and K_2O, 5.01; volatile matter, 5.73 per cent.[1]

Experiment 17.

1.0 gram clay (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

It was ignited by means of a magnesium ribbon. The fusion was quiet. The fused mass dissolved completely in hydrochloric acid, leaving no residue.

Experiments were made with a fire clay of the following composition: SiO_2, 67.37; Al_2O_3, 21.69; Fe_2O_3, 1.59; TiO_2, 1.32; loss on ignition, 8.70 per cent.

Experiment 18.

1.0 gram fire clay (200-mesh sieve).
8.0 grams sodium peroxide.
0.3 gram potassium persulphate.
1.2 grams zinc sulphide.

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[1] This analysis and the one of the fire clay were made by the chemists of the Illinois State Geological Survey.

The above mixture was ignited by means of magnesium ribbon. The melt, when taken up in water and made acid with hydrochloric acid, went into solution completely, leaving no insoluble residue. This method may be used advantageously in connection with the determination of titanium by the method described by one of the authors.[1]

c. Copper Matte.—A copper matte high in copper was used in the following experiments:

Experiment 19.

1.0 gram copper matte (200-mesh sieve).
8.0 grams sodium peroxide.
0.5 gram zinc sulphide.
0.3 gram potassium persulphate.

This mixture was ignited in the usual manner. The mass became very hot and liquid. It was necessary to sift 3 to 4 grams of sodium peroxide into the molten mass to make it dissolve easily. The melt, when taken up in water and acidified with hydrochloric acid, dissolved completely, leaving no residue.

d. Bauxite.—A sample of bauxite containing a considerable amount of iron and titanium oxides was used for the following experiments:

Experiment 20.

0.5 gram bauxite (200-mesh sieve).
8.0 grams sodium peroxide.
1.2 grams zinc sulphide.
0.3 gram potassium persulphate.

Ignited by means of magnesium ribbon. The fusion was good but the decomposition of the ore very poor. Consequently the pyrite mixture was tried.

Experiment 21.

0.5 gram bauxite.
8.0 grams sodium peroxide.
0.5 gram zinc sulphide.
1.0 gram pyrites.

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[1] Walton: "The Colorimetric Determination of Titanium," J. Am. Chem. Soc., **29**, 481 (1907).

Ignited the above mixture by means of a magnesium ribbon. The fusion was extremely hot. Three or four grams of sodium peroxide were sifted into it to make the melt dissolve easily. The melt was dissolved in water acidified with hydrochloric acid. No residue was left, which indicated complete decomposition.

e. Titanium Iron Ore.—For a titanium iron ore, high in iron and titanium, a mixture essentially the same as that used in Experiment 20 was used, but it did not decompose 0.5 gram of the ore (200-mesh sieve).

A fusion of a mixture similar to that used in Experiment 21 completely decomposed 0.5 gram of the ore.

Notes and Precautions.

To ascertain the effect of the fusions on the nickel crucibles, two new crucibles were weighed, and after sixteen fusions had been made in each they were carefully cleaned and weighed again. The crucible weighing originally 18.7683 grams lost 0.2876 gram in 16 fusions. A crucible weighing originally 18.6119 grams lost 0.3363 gram in 16 fusions. This is an average loss in weight of about 0.02 gram for each fusion. When the hot oxidizing nature of the fusions is considered, this is a very slight loss. The fusions were those made with the lead ores, using sodium peroxide and zinc sulphide.

It was found that a piece of twine about an inch long, soaked in alcohol and lighted, can be used for igniting the mixtures instead of magnesium ribbon. This could be used if, for any reason, magnesium was not to be introduced into the mixture.

A finely divided sample was found to be necessary for the sodium peroxide fusions. In the foregoing experiments, with the exception of the ferro-manganese and the lead slag, it was found necessary to pass the substance to be analyzed through a 200-mesh sieve.

Since sodium peroxide often contains small lumps which keep the mixture from igniting or cause incomplete combustion, it is necessary to pulverize this substance before using it.

The different ingredients must be very thoroughly mixed. A partial mixing results in partial decomposition.

All the ingredients *must be perfectly dry*. The mixture is so easily ignited that if there is any moisture present it may react with the sodium peroxide and evolve enough heat to ignite the mixture prematurely.

Conclusion.

From the foregoing experiments it is evident that sodium peroxide, zinc sulphide, and potassium persulphate, when mixed in certain proportions, give a good fusion medium for the decomposition of the substances used in this investigation. In every case the new method gave results as good as those obtained by the standard method. With possibly slight modifications, it could be extended to numerous other substances, a few of which are indicated in the qualitative experiments. This method is particularly applicable to sulphide ores and to substances high in silica, such as glazes and slags. With basic substances, such as franklinite and chrome iron ore, it is necessary to use iron pyrites to get sufficient heat. Pyrite, however, cannot be used in a good many fusions where iron is objectionable, and to fusions of that nature this method cannot be applied.

The chief advantage of the method is the quickness with which decomposition can be accomplished. The entire operation, including mixing, igniting, cooling, and dissolving the melt, takes approximately five minutes. A decomposition by acid takes from half an hour to an hour and a half or even two hours. Moreover, in most cases the nitric or hydrochloric acid must be expelled by evaporating the solution down to sulphuric acid fumes, which necessitates considerable care and usually takes half an hour longer. In the sodium peroxide method sulphuric acid may be used directly for acidifying, which does away with the tedious evaporation.

In the new method the silica present is practically all brought into solution and kept there, so that it does not clog filters and cause other annoyances. The sulphur in sulphide ores and the carbonaceous matter in slags, etc., is easily and completely oxidized by the sodium peroxide method, and the laborious oxidation by means of nitric acid is avoided.

Another advantage arises from the fact that since these fusions are made in nickel crucibles, a saving is made in the amount of platinum ware used.

UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS.

ON THE THEORY OF INDICATORS AND THE REACTIONS OF PHTHALEINS AND THEIR SALTS.

BY S. F. ACREE AND E. A. SLAGLE.

[SECOND COMMUNICATION ON PHTHALEINS.][1]

(We are indebted to the Carnegie Institution of Washington for aid in this work.)

Professor W. R. Orndorff has called our attention to the fact that he has obtained colored salts of trimethylgalleïn[2] and the corresponding tetrachlor derivative. Such substances as *p*-oxydiphenylphthalid,[3] the phenol methyl ester of phenolphthalein,[4] and the corresponding ethyl ester of tetrabromphenolphthalein[5] dissolve in alkalies without color.

Our theory of tautomeric salts takes account of these facts; since we did not discuss in detail this phase, and several others, in the first paper, we take this opportunity to present this point a little more minutely. We have found that the sodium salt of the phenol ethyl ester of fluoresceïn, apparently pure, dissolves in water with a color which, though very decided, is much less intense than that of fluoresceïn salts. Furthermore, this sodium salt dissolves in absolute methyl and ethyl alcohol, giving a very faint color at temperatures from —15° to 0° which increases very decidedly as the temperature is raised to 80°, but decreases again as the temperature is lowered. This sodium salt yields, on alkylation with ethyl iodide in 0.3 N solution of 40 per cent alcohol, at 60°, a mixture of the colorless phenol diethyl ester and the colored quinone diethyl ester.

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[1] Acree: THIS JOURNAL, **39**, 528, 649; Stieglitz: *Ibid.*, **39**, 651.

[2] *Ibid.*, **26**, 97.

[3] Baeyer: Ann. Chem. (Liebig), **354**, 162.

[4] Ber. d. chem. Ges., **40**, 3728.

[5] *Ibid.*, **30**, 177.

Now the failure of some of these salts to give color and the appearance of color in others, as well as the formation of only one ester in some cases and of the two isomeric esters in other cases, is readily explained by our hypothesis. Using the phenol methyl ester of phenolphthalein as an example, we have the salts in the following tautomeric equilibrium, which varies widely with the different analogous compounds, just as do the tautomeric salts of the urazoles:[1]

$$\underset{P}{(CH_3OC_6H_4)(NaOC_6H_4)C(OCOC_6H_4)} \rightleftarrows$$

$$\underset{Q}{(CH_3OC_6H_4)(O:C_6H_4:)CC_6H_4COONa.}$$

In the case of this particular ester in the equation the salt seems to exist practically all as *P* and cannot form the *quinonephenolates* assumed by Stieglitz and by Acree; the solutions give no color and seem to yield only the phenol diester when heated with methyl iodide.[2] In the case of the colored sodium salt of the phenol ethyl ester of fluoresceïn, and of Professor Orndorff's trimethylgalleïn, etc., if these substances in hand are pure the equilibrium conditions must be different, and both *P* and *Q* must be present. *Q* gives color to the solution because (1) it has a quinone group and (2) it unites to a greater or lesser extent with *P* and forms an *intermolecular* quinonephenolate group. The same kind of evidence applies to the dibasic salts of phenolphthalein, fluoresceïn, etc., as was shown on pp. 541–544 of our first article. Mr. Slagle finds that *P* and *Q* yield the two corresponding esters when treated with alkyl halides. The tendency to form *P* and *Q* and the quinonephenolate groups will vary greatly with the different compounds; hence the apparent lack of color in some of the phenol esters of such compounds, as was discussed on p. 531, *et seq.*

Green and King[3] have explained this lack of color on the basis of the hydration of the quinone group:

$$(CH_3OC_6H_4)(HOC_6H_4)C(OCOC_6H_4) + \overset{+}{Na}\overset{-}{OH} \longrightarrow$$

$$(CH_3OC_6H_4)(HOC_6H_4)C(OH)C_6H_4CO\overset{-}{O}\overset{+}{Na}.$$

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[1] Acree: This Journal, **37**, 71; **38**, 1.

[2] Meyer and Spengler: Ber. d. chem. Ges., **38**, 1318.

[3] J. Chem. Soc., **85**, 398. Ber. d. chem. Ges., **40**, 3724

This, without doubt, plays an important part in some cases. But this point of view does not account, in the present case, for the formation of the nearly quantitative yields of the phenol dimethyl esters from methyl iodide and the sodium salts of phenolphthalein and hydroquinonephthalein, nor for the formation of *both* isomeric esters of fluoresceïn obtained by Mr. Slagle; our theory does account for these facts. It is unfortunate that no one has isolated these colorless salts and shown by analysis whether they are hydrated and become colored when dehydrated.

We must be very careful about drawing conclusions concerning the *colors* of these salts, as small amounts of salts of phenolphthalein, fluoresceïn, etc., often give rise to a great part or all of the color actually observed.

JOHNS HOPKINS UNIVERSITY,
April 15, 1908.

REPORT.

RECENT ADVANCES IN CHEMICAL INDUSTRY.

Methods of Combining Atmospheric Nitrogen.

Although the press has announced the discovery of new sodium nitrate deposits in Chili, the final exhaustion of all such deposits is but a question of years, and the problem of providing a cheap and sufficient supply of combined nitrogen is the chief chemical problem of the day.

Bacterial Action.—The work of the German factories and of the U. S. Department of Agriculture in distributing cultures of bacilli suitable for leguminous plants has not as yet proved as great a practical success as was hoped for. Possibly the cultures were not hardy enough. It seems certain, however, that the application of these cultures to seed or soil with favorable results will be a solved problem in the immediate future.

The recent work of Professor Bottomley, of King's College, London—if it should be confirmed by other workers—is most important. Bottomley claims to have developed new physiological varieties of the ordinary bacillus of leguminous plants which are capable of symbiosis with nonleguminous plants. As to his method, in one series of experiments he removed a colony of *bacillus radicicola* from the leguminous root and placed it in an infusion of tomato roots; the bacilli survived this treatment and were bred for ten generations in the tomato root infusion, gradually learning to relish its flavor, so that when soil in which tomatoes were planted was sown with these bacilli, occasional nodules were formed on the tomato roots, with improvement of the crop from these plants. Bottomley adapted in the same manner *bac. radicicola* to cereals, roses, cabbages, and strawberries, and says that in every case root nodules were formed on some plants, with increased yield from these plants.

If this work is confirmed, and it proves possible in time to produce breeds of hardy bacilli which can be *relied* on to produce sufficient nodulizing for all plants, leguminous and non-leguminous, no nitrogenous fertilizers will be needed, and the nitrogen combination problem will be simplified.

Chemical Methods of Combining Atmospheric Nitrogen.

There are three general methods used technically; combining nitrogen with oxygen to yield nitrates or nitrites; nitrogen with carbon and calcium to yield calcium cyanamide; nitrogen with hydrogen to yield ammonia.

Nitrates.—The Birkeland-Eyde process, utilizing the thermal action of the arc on air in a magnetic field to form nitric oxide which is oxidized to nitrogen dioxide and this to nitric acid which is marketed as calcium nitrate, was fully described in THIS JOURNAL[1] at the time of its invention. As predicted, it has proved a practical success. Birkeland has obtained additional patents. The Badische Anilin- and Soda-Fabrik have patents bearing on this process and have established a partnership with the Birkeland-Eyde Company. The fact that a number of patents have been granted in Germany, France, and England on variations of this process, and on attempts to substitute for the magnetic field a mechanical spreading of the contact between arc and air, is further proof of a general belief in the success of the process.

Nitrites.—Nitric oxide in contact with air or oxygen forms nitrogen dioxide. Raschig[2] has, however, proved experimentally that nitrogen trioxide is formed as an intermediate product, and that the reaction velocity of the phase

$$4NO_2 + O_2 = 2N_2O_3$$

(15 seconds) is greater than that of the second phase,

$$2N_2O_3 + O_2 = 4NO_2$$

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[1] THIS JOURNAL, **35**, 358.

[2] Z. ang. Chem., **1905**, 1281.

(60–80 seconds). The Badische Anilin- und Soda-Fabrik find that the second phase can be completely suppressed by keeping the gases at a temperature of about 300°, and have patented a process for making pure nitrites by keeping the gases which leave the Birkeland-Eyde furnace at this temperature, and passing them into solutions of bases which absorb the nitrogen trioxide.

Calcium Cyanamide.—The process of Frank and Caro has proved a commercial success. They conduct nitrogen (obtained by fractioning liquid air) over commercial calcium carbide heated from 750° to 1000° in an electric furnace; the nitrogen instantly reacts on the carbide which glows brightly, forming calcium cyanamide:

$$CaC_2 + N_2 = CN_2Ca + C.$$

Eleven cyanamide factories, with an annual capacity of 166,600 tons, are built or in process of construction in Europe. An "American Cyanamide Co." is building a plant with an annual capacity of 40,000 tons on the Tennessee river, in northern Alabama.

Cost of Combined Nitrogen.—P. A. Guye—who is an expert on this subject—in a lecture before the English Society of Chemical Industry,[1] said that the cost of combining nitrogen by the cyanamide process and by the Birkeland-Eyde process is about the same; he estimates it as about 24 cents per kilogram of nitrogen.

Ammonia from Generator Gas.—Although it is easy to obtain ammonia by the silent discharge in a mixture of pure nitrogen and hydrogen, Berthelot did not succeed in obtaining ammonia by the silent discharge in generator gas, but obtained polymers of formamide, $(HCONH_2)_n$. The Westdeutsche Thomas Werke,[2] however, have patented a process for obtaining ammonia from generator gas. By cooling the gas to 65° to 80° and using a current of 15,000 volts and 2 amperes, they change 20 per cent of the nitrogen in the generator gas into ammonia and market it as ammonium sulphate.

Ammonia and Electric Energy from Peat and from Fuel Waste.—Another method of obtaining ammonia which utilizes both the nitrogen of fuel and that of air and which many inventors are attempting to work out is illustrated in the process of Ward and Sugden,[3] in England, and of Frank and Caro[4] in Germany, for utilizing fuel refuse and peat.

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[1] J. Soc. Chem. Ind., **1906**, 567.

[2] Chem. Ind., **30**, 552.

[3] Elek.-chem. Z., **14**, 84.

[4] *Ibid.*, **14**, 86; and Z. ang. Chem., **19**, 569.

It is realized that all processes based on utilizing peat as transportable fuel by compressing and drying it never have paid and cannot pay, as the volume of the peat is too great, even when compressed, as compared with its fuel value, to repay transportation, so that the consumption must be local. Of course, the idea of transforming the peat *in situ* into electric energy and transporting the energy to factories suitably placed suggested itself to many inventors. Frank and Caro have adopted Ludwig Mond's gas generator to a method for gasifying any kind of cheap fuel in a mixture of air and steam. They are using peat as dug from the bog, containing 50 per cent water, and also the refuse from the coal washers. The product is a fuel gas rich in ammonia. After removing the ammonia the gas is burned in large gas engines, generating power (gas engines of as much as 5000 horse power are used in Germany). Large plants for this process are in construction. It is stated that the yield in ammonia will pay the working expenses and the interest on the capital invested.

Ammonia from Coking Ovens.—Increased attention is now given to obtaining ammonia as a by-product of coking ovens. Indeed, the increased demand in Germany in 1906 for sulphuric acid to convert the ammonia into ammonium sulphate was so great that the domestic supply of acid was insufficient, and increased import was required.

Peat Paper.

Another use of peat is as raw material for wrapping paper and cardboard. An English syndicate working on an American patent has bought a large peat bog in Sweden for this purpose. It is said that the peat is converted into paper in two hours.

Graphite.

The output of artificial graphite by the International Graphite Co., of Niagara Falls, has steadily increased, being 5,074,757 pounds in 1906. Acheson, the inventor of carborundum and of artificial graphite, recently discovered a method of making very soft, pure graphite, and gave attention to utilizing it as a lubricant; he found that by treating the graphite with tannic acid it is changed from the flocculent form to so fine a powder that its emulsion in water passes readily through fine filter paper. He calls it "deflocculated" graphite, and its emulsions in water, in petroleum and in thin mineral oils have the properties of the best lubricators; one or the other of these emulsions forms a suitable lubricator for a given type of machinery. The material is attracting attention here and abroad.

Silicon Monoxide.

Silicon monoxide,[1] SiO, is made by reducing silicon dioxide in the electric furnace by carborundum or carbon:

$$2SiO_2 + SiC = 3SiO + CO.$$

The material is a white solid, is patented under the trade-name "monox," and is used as an adjunct to paints.

Hydrogen.

The use of war balloons in Germany has led the German Government[2] to build works for making and storing hydrogen. The hydrogen is made by the Schuckert system by the electrolysis of a 20 per cent solution of potassium hydroxide at 60° to 70°. To prepare 1 cubic meter of hydrogen requires 6.4 kilowatts of energy. Iron anodes are used; 2 kilograms iron are used up per 100 cubic meters hydrogen. The gas is washed by scrubbers and passes to the gasometers used for filling the balloons, or is compressed in cylinders for storage. One establishment with a capacity for making 1200 cubic meters per 24 hours is completed; another is building.

Cellite.

Dr. Eichengrün, of Elberfeld, has invented a substitute for celluloid, which he calls cellite.[3] It is a cellulose acetate; it can be pressed and moulded like celluloid; is, in thin layers, as flexible as leather, somewhat elastic, transparent and clear, not acted on by water, and incombustible.

Artificial Silk.

The artificial silk manufacturers[4] have improved their product recently by employing a cellulose acetate, which gives a more durable fabric than that first marketed.

Sulphur.

The present position of the Louisiana and Italian sulphur industry in relation to the world's supply of sulphur is very interesting. As is generally known, the Louisiana sulphur is in a deep-lying bed, and is obtained by the Frasch process; superheated steam is forced through pipes into the bed, melting the sulphur and forcing the molten sulphur to the surface in practically pure form. In round numbers, the Louisiana production in 1904 was 129,500 metric tons, in 1905 185,000, and in 1906 299,000. The production of Sicilian sulphur in 1905 was 569,000 metric tons, and in 1906 500,000.[1] It is estimated that the world's annual demand for sulphur (not including pyrite) is 500,000+ metric tons. The Louisiana deposit is estimated at 40,000,000 metric tons, and the possible production with the present plant is 3000 metric tons daily, or 900,000 yearly.[2] One hundred and fifty-six thousand metric tons of Sicilian sulphur were imported into the United States in 1893. The import shrunk to 41,000 metric tons in 1906.

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[1] Elek.-chem. u. metallurg. Ind., **1907**, 442.

[2] Elek.-chem. Z., **14**, 231 (1907).

[3] Chem. Ind., **30**, 476.

[4] *Ibid.*

The Anglo-Sicilian Co., which controlled the Sicilian sulphur production, not believing in the possibilities of the Frasch process, allowed 400,000 metric tons sulphur to accumulate, for which they could find no market; the company liquidated in August, 1906. To prevent the ruin of the Sicilian sulphur industry, which supports a great part of the population, the Italian Government has taken measures not only remarkable but unique in the relations of modern governments to industry.[3] The government bought the sulphur from the company for a price reported as $12.00 per metric ton, and made a law which unites the Sicilian mine owners to a compulsory syndicate, the "Consorzio obbligatorio per l' Industria Zolfifera." By the terms of this law a 50 per cent reduction of the former railroad freight on sulphur is granted, and only syndicate sulphur is allowed to be transported in or exported from Sicily at any price. In this way Italy hoped to meet American rivalry.

Not content with driving Sicilian sulphur from the American market, the Union Sulphur Co. (financed by the Standard Oil Co.) seems determined to monopolize the entire sulphur industry, and is offering American sulphur at Marseilles and Antwerp at $13.00 per metric ton, $20.00 being the average Marseilles price for Sicilian sulphur. American sulphur in New York costs $22.00 to $22.25, and is said by G. Lunge[4] to cost only $2.90 to the producers.

Foreign journals consider the situation very serious, and say that it is impossible for the Sicilian mines, which are surface workings, to compete against sulphur which can be mined by the Frasch process.

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[1] Mineral Resources of U. S., **1906**, 1103.

[2] G. Lunge, in Z. ang. Chem., **1905**, 1009.

[3] Chem. Ind., **30**, 473 and 505 (1907).

[4] Z. ang. Chem., **1905**, 1009.

Steel.

In the manufacture of steel the increasing use of the electric furnace, particularly for making ferro-alloys and high-grade steels, is the point of greatest interest.

To understand the importance of these new steels it should be borne in mind that it is believed that there are three allotropic modifications of steel. It is assumed that there are three allotropic modifications of *iron*, α-, β-, γ-ferrites. Ordinary mild carbon steel is very soft at temperatures below 710° and is in the so-called α condition, in which the carbon is present as a carbide, Fe_3C (cementite), mixed with pure soft iron (α-ferrite). At temperatures between 710° and 810° the steel is in the β or martensite condition, very hard, the carbide going into solid solution in the β-ferrite. Above 810° the steel is in the γ, or austenite condition, in which the carbide is dissolved in γ-ferrite; it is moderately soft and extremely tough. These stages are reversed by slow cooling. If highly heated or molten steel is cooled suddenly or "chilled" it remains in the martensite or β condition at ordinary temperatures. If chilled steel is tempered, it is more or less changed at will in the direction of the α condition, and retains the desired properties at ordinary temperatures. But chilled steel is a supercooled solid solution, and both chilled and tempered steel are in a condition of unstable equilibrium which tends to revert through friction, heat, or jarring, to the normal α condition.

By alloying steel with one or more other elements—such as nickel, chromium, manganese, tungsten, etc., the transformation temperatures are lowered in proportion to the percentage of new element introduced, until the martensite or β form becomes that of stable equilibrium at ordinary temperature (self-hardening steel).

Such steel retains its hardness at temperatures much higher than ordinary steel, it does not lose its hardness ("temper") through frictional heat, and is used under the name of "high-speed" steel for tools. A steel containing 6 to 7 per cent chromium and either 20 to 25 per cent tungsten or 10 to 12 per cent molybdenum is a standard high-speed steel.

A still greater increase in the percentage of new metal makes the γ or austenite condition the stable one at ordinary temperature, forming exceedingly tough steel (automobile steels).

The electric furnace is exclusively used in making the ferro-alloys employed in steel making, such as ferro-silicon containing 25 to 90 per cent silicon; ferro-chrome, with 65 per cent chromium; ferro-molybdenum with 80 per cent molybdenum; silico-manganese with 60 to 70 per cent manganese and 20 to 25 per cent silicon; and many others.

The use of various modifications of the Siemens-Martin open-hearth steel furnace, heated by the arc—each variety bearing the name of its inventor—is greatly increasing for the manufacture of high-grade steel; it is found that the high temperature of the furnace heated by the arc is required to obtain the best results with the β- and γ-steels. Under the general name "steel," alloys are now in use which we should have considered impossible a few years ago, such as the high-speed steels referred to above, or automobile steel containing 30 to 50 per cent nickel.

The study of the special properties imparted to steel by the addition of different amounts of each foreign element, or by addition of more than one foreign element, is most important; and the results already obtained are very interesting; but the subject is too detailed to be reviewed in a brief report.

E. RENOUF.

REVIEWS.

A HISTORY OF CHEMISTRY. By HUGO BAUER. Translation by R. V. STANFORD. New York: Longmans, Green & Co.; London: Edward Arnold. 1907. pp. 232. Price, $1.

This small volume will be of value to students of chemistry as an introduction to larger works on the history of chemistry. The history of a science cannot be treated in an elementary way, as it necessarily has to do with the most important advances in the subject. Only one who has a good knowledge of chemistry can follow the history of chemistry. Nevertheless, it is well for students in the early stages of their work to make an effort to learn what the important steps have been in the progress of their subject and to learn something about the leaders whose work has made the science what it now is. It is obvious that a beginner cannot, for example, make much out of a chapter dealing with the Theory of Nuclei and the Theory of Types, but he can read what is said of these subjects, and if he is rightly constituted he will keep at it, and some time the subject will clear up in his mind. To quote from the volume before us: "Recently the effort has also made itself felt to give life to the study of the history of chemistry by the publication of collections of important original researches, or of the correspondence of the earlier chemists. In this connexion the chief credit is due to W. Ostwald and

J. Kahlbaum. In the same way these pages, which can only present a short and incomplete course through the history of chemistry, may furnish an incitement to young chemists and students of chemistry to penetrate further into the origins and growth of chemical science."

The book can be heartily recommended for the purpose for which it was prepared. I. R.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE. Von WILLIAM A. NOYES. Mit Genehmigung des Verfassers ins Deutsche übertragen von WALTER OSTWALD und mit einer Vorrede von PROFESSOR WILHELM OSTWALD. Leipzig: Akademische Verslagsgesellschaft m. b. H. 1907. pp. 722.

A review of the original American edition of the book before us has already appeared in THIS JOURNAL. The author is to be congratulated on the appearance of this German edition prepared by Walter Ostwald, a son of the distinguished Professor Wilhelm Ostwald. The work of translation was probably undertaken at the instigation of Professor Ostwald, who has written an introduction in which he speaks in very complimentary terms of the book of Professor Noyes. His opinion can best be given in his own words: "Durch die eigenartige Anordnung des Stoffes ist es nun in der Tat möglich geworden, eine solche Symmetrie und Übersichtlichkeit des gesamten Materials herbeizuführen, dass der Student, welcher dieses kleine Buch kennen gelernt hat, seine weiteren Studien mit dem Vertrauen fortsetzen kann, dass er sich in dem Walde der organischen Chemie nicht mehr verirren wird. Dabei hat der Verfasser die unter solchen Umständen besonders schwierige Aufgabe gelöst, dem Schüler die Weite der von ihm künftig noch zu durchmessenden Gebiete zum Bewusstsein zu bringen, ohne ihm den Mut hierzu zu nehmen. Das Mittel hierzu ist die grosse Klarheit der Darstellung, welche den Schüler im gegebenen ganz zu Hause sich fühlen lässt, und ihm so das Vertrauen gibt, auch das Übrige noch bewältigen zu können." I. R.

DESCRIPTIVE BIOCHEMIE mit besonderer Berücksichtigung der chemischen Arbeitsmethoden. By SIGMUND FRÄNKEL. Wiesbaden: J. F. Bergmann. 1907. pp. 639. Price, M. 17.

The volume under consideration aims at fulfilling the functions of a "Beilstein" for biological chemists in which full descriptions of the various substances likely to be encountered will be found. In addition the book contains a mass of useful information concerning analytical and preparative methods and some account is given of the enzymes and the reactions with which they are concerned. The value of a work of this character depends largely upon its completeness and upon the care taken in its compilation, and as a whole, the volume is deserving of high praise and indeed it has already won for itself a position among the most useful books in the biochemical laboratory.

Full references to the literature are furnished throughout and the author has taken the trouble to incorporate a considerable amount of work other than that of Teutonic origin. A glance at a volume of this kind would do much to convince the "pure chemist" of the fact that his physiological brethren are no longer content to work with "messes" and that an ever increasing portion of his work deals with definite substances capable of isolation in pure form.

Dr. Fränkel is to be congratulated on having produced a most admirable book. H. D. DAKIN.

UNTERSUCHUNGEN ÜBER DIE GALVANISCHE LEITFÄHIGKEIT DER ELEKTROLYTE. Von SVANTE ARRHENIUS am 6 Juni, 1883, der kgl. schwedischen Akad. der Wissenschaften vorgelegte Abhandlung. Uebersetzt von ANNA HAMBURGER und herausgegeben von OTTO SACKUR. Mit 6 Figuren im Text. Leipzig: Verlag von Wilhelm Engelmann. 1907. pp. 153. Price, M. 2.50.

This epoch-making paper by Arrhenius is now translated into German and published as Ostwald's Klassiker der exakten Wissenschaften, Nr. 160. As is well known, this is one of the few great contributions which founded the modern science of physical chemistry. Physical chemistry has grown up from a few comprehensive generalizations: The Law of Mass Action; The Relation between Gas Pressure and Osmotic Pressure; The Theory of Electrolytic Dissociation; Faraday's Law as the Basis of Valence; and the Phase Rule.

This earlier work by Arrhenius was the forerunner of the theory of electrolytic dissociation, and it is now placed among the great classics of science where it undoubtedly belongs.

H. C. J.

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FORMULAS.

C_1-GROUP.

1 II.

CH_3I. Methyl iodide. *Acree* and *Shadinger*.................. 275

C_2-GROUP.

2 III.

C_2H_4OS. Thioacetic acid. Na. *Acree* and *Shadinger*........... 273

C_3-GROUP.

3 II.

$C_3H_2N_2$. Malonic nitrile. Na. *Hessler*...................... 76

3 III.

$C_3H_3O_3N$. Nitromalonic aldehyde. *Hale* and *Robertson*.......... 680

C_5-GROUP.

5 I.

C_5H_{10}. Propylethylene. *Clarke*.............................. 91

5 II.

$C_5H_{10}O$. Methyl-*n*-propyl ketone. *Clarke*.................... 89
$C_5H_{11}I$. 2-Iodopentane. *Clarke*............................ 90
$C_5H_{12}O$. Methyl-*n*-propylcarbinol. *Clarke*.................... 89

C_6-GROUP.

6 II.

$C_6O_2Cl_4$. Tetrachlor-*o*-quinone. *Jackson* and *Carleton*.......... 493
$C_6O_2Br_4$. Tetrabrom-*o*-quinone. *Jackson* and *Flint*............ 83
$C_6H_{10}O_2$. Acetonylacetone. *Hale* and *Robertson*................ 680

6 III.

$C_6HO_3Br_3$. Tribromoxy-*p*-quinone. *Jackson* and *Flint*.......... 86
$C_6H_6O_2N_2$. *o*-, *m*-, and *p*-Nitranilines. Hg. *Jackson* and *Peakes*. 570

C_8-GROUP.

8 I.

C_8H_{18}. (1) Diethylisopropylmethane. *Clarke*...........572, 575, 578
(2) Methyldi-*n*-propylmethane. *Clarke*..................... 87, 96

8 II.

$C_8H_{16}O$. (1) β-Amylacetone (4-methyl-2-heptanone). *Clarke*.. 93
(2) 3-Isopropyl-2-pentanone. *Clarke*...................... 577
$C_8H_{17}I$. (1) 3-Ethyl-2-methyl-2-iodopropane. *Clarke*.......... 575
(2) 2-Iodo-4-methylheptane. *Clarke*....................... 95
(3) 3-Isopropyl-2-iodopentane. *Clarke*.................... 578
$C_8H_{18}O$. (1) 3-Ethyl-2-methyl-2-pentanol. *Clarke*............ 574
(2) 3-Isopropyl-2-pentanol. *Clarke*........................ 578
(3) 4-Methyl-2-heptanol. *Clarke*........................... 94

8 III.

$C_8H_7O_2N_3$. Phenylurazole. Ag (p. 134), Na (p. 131). *Acree* and *Shadinger*.. 131
$C_8H_7O_4Br_3$. Tribrommethoxy-*o*-quinonemethylhemiacetal. *Jackson* and *Flint*.. 83
$C_8H_7O_5N$. 5-Nitro-2-methoxybenzoic acid. *Hale* and *Robertson* 688
$C_8H_8O_3N_2$. Methyl imido-*m*-nitrobenzoate. *Derby*............447, 473
Schlesinger......... 759
+ HCl. *Derby*.....454, 463
C_8H_9ON. Methyl imidobenzoate. *Derby*....................445, 472
Schlesinger................744, 768
+ HCl. *Derby*......449, 461, 465, 470
Schlesinger.......... 733
C_8H_9ON. *o*-Methylbenzamide (amide of toluic acid). Ag. *McCracken*.. 603

8 IV.

$C_8H_7ON_3S$. 1-Phenyl-3-thiourazole. Ba (pp. 142, 263); Mg (p. 263); Na (pp. 140, 260, 264, 273, 275). *Acree* and *Shadinger*..139, 271

C_9-GROUP.

9 II.

$(C_9H_5N_2)_x$. (1) Product of addition of bromine to sodium phenylmalonic nitrile. *Hessler*.......... 69
(2) Product of oxidation of phenylmalonic nitrile and its polymers by chromic acid. *Hessler*.......... 67
$(C_9H_5N_2)_x$ or $(C_9H_6N_2)_x$. (1) Product of addition of sodium phenylmalonic nitrile to bromine. *Hessler*.......... 70
(2) Product of reaction of sodium phenylmalonic nitrile with benzenediazonium chloride. *Hessler*.......... 74
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$C_9H_8O_3$. Phenylpyroracemic acid. *Hessler*.......... 80
$C_9H_{10}O_4$. Veratric acid. *Clarke* and *Jackson*.......... 717

9 III.

C_9H_7OCl Cinnamyl chloride. *Michael* and *Smith*.......... 26
$C_9H_7OCl_3$. (1) Cinnamyl chloride allodichloride. *Michael* and *Smith*.......... 26
(2) Cinnamyl chloride dichloride. *Michael* and *Smith*.......... 26
$C_9H_7O_2N$. Phenylcyanacetic acid. *Hessler*.......... 77
$C_9H_8ON_2$. Phenylcyanacetamide. *Hessler*.......... 74, 77
$C_9H_8O_2Cl_2$. (1) Cinnamic acid allodichloride. *Michael* and *Smith* 22
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$C_9H_8O_6N_2$. 2-Acetonyl-4,6-dinitrophenol. *Hale* and *Robertson*.. 688
$C_9H_9O_2N_3$. (1) 1-Phenyl-2-methylurazole. Na (p. 132). *Acree* and *Shadinger*.......... 133
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$C_9H_{10}O_3N_2$. Ethyl imido-*m*-nitrobenzoate. + HCl. *McCracken*. 607
$C_9H_{11}ON$. (I) Ethyl imidobenzoate. *Derby*.......... 442, 472
Schlesinger.......... 750
+ HCl. *Derby*..449, 455, 460, 466, 470
McCracken.......... 591
Schlesinger.......... 722
(2) Methyl imido-*o*-toluylate. + HCl. *McCracken*.......... 603

9 IV.

$C_9H_9ON_3S$. (1) 1-Phenyl-3-methylthiourazole. Na (p. 141). *Acree* and *Shadinger* 141
(2) 1-Phenyl-4-methyl-3-thiourazole. *Acree* and *Shadinger* 140
$C_9H_{10}ONBr$. Ethyl imido-*m*-brombenzoate. + HCl. *McCracken* 609

C$_{10}$-GROUP.

10 I.

$C_{10}H_{16}$. (1) Limonene. *Clover* 630
(2) *α*-Phellandrene. *Clover* 634

10 II.

$C_{10}H_8N_2$. Methylphenylmalonic nitrile. *Hessler* 73
$C_{10}H_{10}O_2$. Methyl cinnamate. *Michael* and *Smith* 25, 28
$C_{10}H_{18}O_2$. Auto-oxidation product of phellandrene. *Clover* 640
$C_{10}H_{18}O_3$. Ethyl diethylacetacetate. *Clarke* 574

10 III.

$C_{10}H_6O_5Br_3$. Tribrommethoxy-*o*-quinonemonomethylacetacetal. *Jackson* and *Flint* 85
$C_{10}H_{10}O_2Cl_2$. (1) Methyl cinnamate allodichloride. *Michael* and *Smith* 25
(2) Methyl cinnamate dichloride. *Michael* and *Smith* 25
$C_{10}H_{10}O_2Br_2$. (1) Methyl cinnamate allodibromide. *Michael* and *Smith* 28
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$C_{10}H_{11}O_4N$. 2-Acetonyl-4-nitromethoxybenzene. *Hale* and *Robertson* 686, 687
$C_{10}H_{13}ON$. (1) Ethyl imidophenylacetate. + HCl. *McCracken* 605
(2) Ethyl imido-*p*-toluylate. + HCl. *McCracken* 602
(3) Isopropyl imidobenzoate. *Derby* 446, 473
Schlesinger 756
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Schlesinger 753
+ HCl. *Derby* 453, 463
$C_{10}H_{16}O_3N_2$. *α*-Phellandrene *α*-nitrite. *Clover* 635

10 IV.

$C_{10}H_{11}ON_3S$. 1-Phenyl-3-ethylthiourazole. *Acree* and *Shadinger* 142

C_{11}-GROUP.

11 II.

$C_{11}H_{12}O_2$. Ethyl cinnamate. *Michael* and *Smith* 27

$C_{11}H_{16}O_4$. By-product in reaction between sodium ethyl acetacetate and 2-iodopentane. *Clarke* 91

$C_{11}H_{20}O_3$. (1) Ethyl β-amylacetacetate. *Clarke* 92

(2) Ethyl ethylisopropylacetacetate. *Clarke* 576

11 III.

$C_{11}H_{11}O_2N$. Ethyl phenylcyanacetate. *Hessler* 74, 77

$C_{11}H_{12}O_2Br_2$. Ethyl cinnamate allodibromide. *Michael* and *Smith* 27

$C_{11}H_{12}O_6N_2$. 2-Acetonyl-4,6-dinitroethoxybenzene. *Hale* and *Robertson* 689

$C_{11}H_{13}O_2N_3$. 1-Phenyl-3-ethoxy-4-methylurazole. *Acree* and *Shadinger* 143, 144

$C_{11}H_{13}O_4N$. 2-Acetonyl-4-nitroethoxybenzene. *Hale* and *Robertson* 687

$C_{11}H_{14}O_4N_2$. 2-Acetoxime-4-nitroethoxybenzene. *Hale* and *Robertson* 688

$C_{11}H_{15}ON$. Isobutyl imidobenzoate. + HCl. *McCracken* 598

C_{12}-GROUP.

12 II.

$C_{12}H_6O_4$. Diquinone. *Hale* and *Robertson* 692

$C_{12}H_{10}O_4$. Dihydroquinone. *Hale* and *Robertson* 693

$C_{12}H_{22}O_{11}$. Cane sugar. *Morse* and *Morse* 667

12 III.

$C_{12}HO_4Cl_7$. Heptachlor-*o*-quinopyrocatechin hemiether. *Jackson* and *Carleton* 499

$C_{12}H_2O_4Cl_8$. Octochlor-*o*-quinhydrone. *Jackson* and *Carleton* 497

$C_{12}H_8O_6N_2$. 3,3′-Dinitro-6,6′-dioxydiphenyl. *Hale* and *Robertson* 690

$C_{12}H_{11}O_3N$. Ethyl phenylcyanpyroracemate. *Hessler* 77

$C_{12}H_{12}O_2N_2$. 3,3′-Diamino-6,6′-dioxydiphenyl. *Hale* and *Robertson* 692

$C_{12}H_{15}O_2N_3$. 1-Phenyl-3,5-diethoxyurazole. *Acree* and *Shadinger* 136, 144

$C_{12}H_{17}ON$. Isoamyl imidobenzoate. + HCl. *McCracken* 601

C_{13}-GROUP.

13 III.

$C_{13}H_4O_5Cl_6$. Hexachlor-*o*-quinomethylmonohemiacetalpyrocatechin ether. *Jackson* and *Carleton*...................... 501
$C_{13}H_{13}ON$. Ethyl imido-β-naphthoate. + HCl. *McCracken*...... 609
$C_{13}H_{21}ON$. Ethylcamphoformeneamine. *Tingle* and *Williams*.. 288

C_{14}-GROUP.

14 II.

$C_{14}H_{14}O_4$. (1) Curcumine. *Clarke* and *Jackson*.................. 711
(2) Rosocyanine. Ba (p. 709); NH_4 (p. 708); K (p. 708). *Clarke* and *Jackson*.................................... 696
(3) Rubrocurcumine. *Clarke* and *Jackson*.................. 711

14 III.

$C_{14}H_8O_6Cl_6$. Hexachlor-*o*-quinomethylhemiacetalpyrocatechin ether. *Jackson* and *Carleton*............................ 502
$C_{14}H_{12}O_6N_2$. (1) 3,3′-Dinitro-6,6′-dimethoxydiphenyl. *Hale* and *Robertson*.. 694
(2) 3,3′-Dinitro-3-oxy-3′-ethoxydiphenyl. *Hale* and *Robertson* 695
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C_{15}-GROUP.

15 II.

$C_{15}H_{16}O_4$. (1) Methylcurcumine. *Clarke* and *Jackson*.......... 716
(2) Methylrosocyanine. *Clarke* and *Jackson*................. 718
$C_{15}H_{26}O$. Product obtained from a sample of Manila elemi. *Clover*.. 645

15 III.

$C_{15}H_6O_6Cl_6$. Hexachlor-*o*-quinomonomethylacetacetalpyrocatechin ether. *Jackson* and *Carleton*...................... 501
$C_{15}H_{12}ON_2$. Phenylcyanacetanilide. *Hessler*.................. 75
$C_{15}H_{13}ON_3$. Phenylcyanacetic acid phenylhydrazide. *Hessler*.. 76
$C_{15}H_{25}O_4N$. Trimethylamine camphoroxalate. *Tingle* and *Williams*.. 293

C_{16}-GROUP.

16 II.

$C_{16}H_{16}O_5$. (1) Acetrosocyanine. *Clarke* and *Jackson*........... 710
(2) Acetrubrocurcumine. *Clarke* and *Jackson*................ 713

16 III.

$C_{16}H_{14}ON_2$. Phenylcyanacettoluidides (*o*-, *m*-, and *p*-). *Hessler*. 76

$C_{16}H_{16}O_6N_2$. 3,3′-Dinitro-6,6′-diethoxydiphenyl. *Hale* and *Robertson* 694

$C_{16}H_{28}O_3N_2$. Ethylamine ethylcamphoformeneaminecarboxylate. *Tingle* and *Williams* 288

16 IV.

$C_{16}H_{15}O_4N_2Br_3$. Tribrommethoxy-*o*-quinonemonomethylacetacetalhydrazone. *Jackson* and *Flint* 85

C_{17}-GROUP.

17 III.

$C_{17}H_{20}O_3N_2$. *p*-Nitrophenylcamphoformeneamine. *Tingle* and *Williams* 290

$C_{17}H_{21}O_2N$. *p*-Hydroxyphenylcamphoformeneamine. *Tingle* and *Williams* 292

C_{18}-GROUP.

18 II.

$C_{18}H_{12}N_4$. Dimolecular phenylmalonic nitrile. Ag (p. 71). + Benzene (p. 66). *Hessler* 65

18 III.

$C_{18}H_{19}O_3N$. *o*-Hydroxyphenylcamphoformeneaminecarboxylic acid lactone. *Tingle* and *Williams* 290

$C_{18}H_{21}O_3N$. Phenylcamphoformeneaminecarboxylic acid. *Tingle* and *Williams* 297

$C_{18}H_{21}O_4N$. *p*-Hydroxyphenylcamphoformeneaminecarboxylic acid. *Tingle* and *Williams* 292

$C_{18}H_{23}ON$. Phenylmethylcamphoformeneamine. *Tingle* and *Williams* 118

$C_{18}H_{31}O_4N$. Triethylamine camphoroxalate. *Tingle* and *Williams* 294

C_{19}-GROUP.

19 III.

$C_{19}H_{24}O_2N_2$. Acetylphenylaminecamphoformeneamine. *Tingle* and *Williams* 120

$C_{19}H_{25}ON$. Phenylethylcamphoformeneamine. *Tingle* and *Williams* 118

$C_{19}H_{33}ON$. Diisobutylcamphoformeneamine. *Tingle* and *Williams* 114

C_{20}-GROUP.

20 II.

$C_{20}H_{16}N_4$. Ethyl dimolecular phenylmalonic nitrile. *Hessler*... 71

20 III.

$C_{20}H_{27}ON$. Benzylethylcamphoformeneamine. *Tingle* and *Williams*... 119

$C_{20}H_{34}O_3N$. Diisobutylisocamphoformolaminecarboxylic acid. *Tingle* and *Williams*... 114

C_{21}-GROUP.

21 III.

$C_{21}H_{29}O_4N$. Benzylethylisocamphoformolaminecarboxylic acid. *Tingle* and *Williams*... 119

$C_{21}H_{37}ON$. (1) Diamylcamphoformeneamine. *Tingle* and *Williams*... 116

(2) Diisoamylcamphoformeneamine. *Tingle* and *Williams*. 116

C_{22}-GROUP.

22 II.

$C_{22}H_{20}N_4$. *n*-Butyl dimolecular phenylmalonic nitrile. *Hessler*. 72

22 III.

$C_{22}H_{39}O_4N$. (1) Diamylisocamphoformolaminecarboxylic acid. *Tingle* and *Williams*... 115

(2) Diisoamylisocamphoformolaminecarboxylic acid. *Tingle* and *Williams*... 116

C_{24}-GROUP.

24 III.

$C_{24}H_{30}O_6N_2$. *p*-Aminophenol *p*-hydroxyphenylcamphoformolaminecarboxylate. *Tingle* and *Williams*... 291

C_{25}-GROUP.

25 III.

$C_{25}H_{29}ON$. Dibenzylcamphoformeneamine. *Tingle* and *Williams* 117

C_{27}-GROUP.

27 II.

$C_{27}H_{18}N_6$. Trimolecular phenylmalonic nitrile. *Hessler*... 67

C_{31}-GROUP.

31 III.

$C_{31}H_{40}O_6N_2$. Quinine camphoroxalate. *Tingle* and *Williams*.. 295

C_{33}-GROUP.

33 III.

$C_{33}H_{38}O_6N_2$. Strychnine camphoroxalate + 0.5 mol. ethyl acetate. *Tingle* and *Williams*.............................. 295

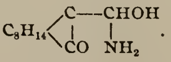
C_{34}-GROUP.

34 III.

$C_{34}H_{42}O_9N_2$. Brucine camphoroxalate. *Tingle* and *Williams*.. 296

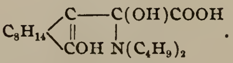
ERRATA.

Volume 34, page 578, line 10,[1] insert TINGLE, ALFRED. Phenylisoxazolone, 471.
" 34, " 608, " 10, for 371 read 471.
" 34, " 617, " 7, insert $C_9H_7O_2N$. Phenylisoxazolone. *Tingle*, 471.
" 35, " 554, " 12, insert *Robinson, C. J.* Combustion of halogen compounds in presence of copper oxide, 531.
" 35, " 557, " 2, insert Combustion of halogen compounds in presence of copper oxide. *Robinson*, 531.
" 36, " 283, last line, for 36 read 35.
" 39, " 105, line 3,[1] insert J. Am. Chem. Soc., 29, 1242 (1907).
" 39, " 108, formula for camphoformolamine should read



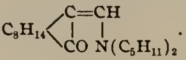
$$C_8H_{14}\left\langle\begin{matrix}C—CHOH\\ |\qquad\ |\\ CO\quad NH_2\end{matrix}\right. .$$

" 39, " 109, line 5, formula should read



$$C_8H_{14}\left\langle\begin{matrix}C——C(OH)COOH\\ \|\qquad\ |\\ COH\ N(C_4H_9)_2\end{matrix}\right. .$$

" 39, " 109, " 24, formula should read



$$C_8H_{14}\left\langle\begin{matrix}C{=}CH\\ |\quad\ |\\ CO\ N(C_5H_{11})_2\end{matrix}\right. .$$

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[1] From bottom of page.

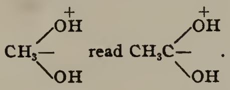
Volume 39, page 143, line 3, for

$$= K \frac{\alpha^2}{(1-\alpha)\sqrt{V}} \text{ read } K = \frac{\alpha^2}{(1-\alpha)\sqrt{V}}.$$

" 39, " 146, " 4,[1] transpose the numbers 335, 338, 339, and 342 to end of next line.

" 39, " 149, " 12, after Dietz, omit lines 12, 13, and 14.

" 39, " 151, " 14 and 18, for



" 39, " 229, interchange subjects in sections 6 and 7.

" 39, pages 245 and 246, for K_{trans} in equations (4), (6), and (7)

$$\text{read } \frac{K_{trans}}{K_{equil}}.$$

" 39, page 247, line 9, omit K.

" 39, " 276, " 3[1], for $CH_3C\rightleftarrows$ read $CH_3CH\rightleftarrows$.

" 39, " 431, " 12, for T. B. COHEN read J. B. COHEN.

" 39, " 528, line 3, after BY S. F. ACREE insert AND JULIUS STIEGLITZ.

" 39, " 753, " 18, insert NEUMANN, B. Elektrometallurgie des Eisens (Review), 509.

" 39, " 760, " 10, insert Eisens, Elektrometallurgie des. *Neumann*, 509.

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[1] From bottom of page.

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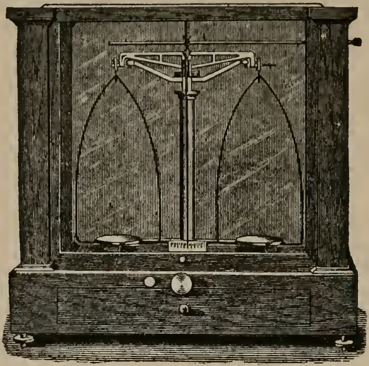

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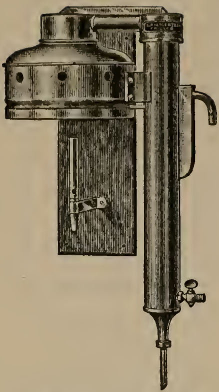

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